

## GWERD QUALITY ASSURANCE PROJECT PLAN

TITLE: Ground-Water Investigation in Pavillion, Wyoming

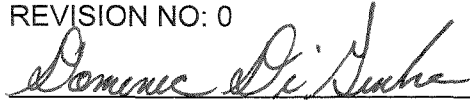

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## 1.0 Project Description and Objectives

### 1.1 Process and/or Environmental System to be Evaluated

This investigation is being conducted to provide technical support to EPA Region VIII to complete a ground-water investigation near Pavillion, Wyoming under authority of the Comprehensive Environmental Response, Compensation, and Liability Act. EPA Region VIII is lead organization of this investigation. The investigation was initiated in response to complaints about odors and taste associated with water in domestic wells. Potential sources of ground-water contamination include activities associated with oil and gas production such as leaking or abandoned pits, gas well completion and enhancement techniques, improperly plugged and abandoned wells, as well as activities associated with residential or agricultural practices. EPA Region VIII has completed two phases of domestic well sampling in addition to collecting surface water and soil samples to determine potential sources of contamination in the area which include but are not restricted to natural gas development

### 1.2 Purpose of the Project and Specific Project Objectives

NRMRL-Ada will assist EPA Region VIII in this investigation by: (1) installing two deep monitoring wells in two areas where contamination is suspected, (2) sampling these wells as well as from a subset of existing domestic wells, (3) providing samples to the EPA Region VIII laboratory for analysis of organic compounds, (4) analyzing ground-water samples for major ions, inorganic compounds, metals and dissolved gases at NRMRL-Ada's laboratory in Oklahoma as well as stable isotopes of dissolved inorganic carbon at Isotech Laboratories, (5) conducting a soil-gas survey using the Geoprobe Post Run Tube (PRT) System and screening samples in the field for fixed gases and total hydrocarbons using portable gas analyzers, and (6) installing dedicated soil-gas probes and collecting samples for analysis of fixed gases, light hydrocarbons, and isotopes at a Istotech Laboratories. A tentative schedule of field activities is provided in **Table 1**.

In addition to assisting EPA Region VIII in this investigation, field activities at this site will assist NRMRL-Ada in understanding the transport of gases in deep subsurface media and associated geochemical reactions in ground water. While carbon dioxide (CO<sub>2</sub>) is not a gas of concern in the Pavillion area, subsurface conditions at Pavillion serve as an anthropogenic analogue for study of geologic sequestration of CO<sub>2</sub>. Geological sequestration is recognized as the injection and subsequent long-term trapping of gaseous, liquid, or supercritical CO<sub>2</sub> in subsurface media – primarily saline formations, depleted or nearly depleted oil and gas reservoirs, and coal seams. Carbon capture, transport, and storage via geologic sequestration from stationary sources of CO<sub>2</sub> such as refineries, and coal-fired electric, ethanol, cement, and fertilizer plants could allow continued use of fossil fuels in a manner that greatly reduces CO<sub>2</sub> emissions until alternative energy sources are deployed on a large scale in the coming decades.

One research objective of this study is to evaluate the feasibility of using soil-gas measurements to detect the migration of gases from deep subsurface media. It is widely acknowledged that leakage through transmissive faults (and associated fractures) and well penetrations (operational, non-operational, and abandoned wells) are the most likely potential pathway for CO<sub>2</sub> release from a storage formation at a properly selected site for geologic sequestration. Leakage through transmissive faults and well penetrations could result in intrusion of CO<sub>2</sub> or brine into underground sources of drinking water (USDWs), release of CO<sub>2</sub> to the vadose zone and the atmosphere, and intrusion of CO<sub>2</sub> into buildings. Release of CO<sub>2</sub> or

brine into a USDW could be accompanied by measurable alteration in pH, major ions, and mobilization of hazardous inorganics. Release of CO<sub>2</sub> into the vadose zone could be accompanied by compositional changes in soil gas and flux to the atmosphere. Release of CO<sub>2</sub> into buildings could result in increased CO<sub>2</sub> and potential reduction in oxygen in indoor air. The area of investigation near Pavillion has a large number of well penetrations (production and abandoned wells) under pressure similar to enhanced oil recovery. Also, stimulation of gas production wells may have resulted in fracture networks in deep subsurface media deposits similar to that which would occur near faults. If a soil-gas survey at this site identifies anomalies of light hydrocarbons and gases, it is likely that soil-gas sampling will be an effective technology for monitoring and verifying storage of CO<sub>2</sub> at a site much more suitable for storage of CO<sub>2</sub>.

Another research objective of this study which is relevant to geologic sequestration is to develop a sampling methodology that allows collection of ground-water samples approaching or in excess of 1000' below ground surface while retaining dissolved gases. Dissolved gases such as CH<sub>4</sub> and CO<sub>2</sub> off gas during ground-water sample retrieval using conventional methodologies.

## **2.0 Organization and Responsibilities**

### **2.1 Identification of Key Personnel and Responsibilities**

*Dr. Dominic DiGiulio*, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. DiGiulio is the principal investigator of this project and is responsible for ensuring completion of all aspects of this QAPP. He will lead the collection, analysis, and interpretation of soil-gas samples. He is the work assignment manager for overseeing the installation of monitoring wells. His COR certification is current. He is the Health and Safety Officer for soil-gas sampling activities carried out by NRMRL-Ada. His HAZWOPER certification is current.

*Dr. Richard Wilkin*, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Wilkin is a co-principal investigator for this project. He will lead all aspects of this investigation related to the collection, analysis, and interpretation of ground-water samples. He is the Health and Safety Officer for ground-water sampling activities carried out by NRMRL-Ada. His HAZWOPER certification is current.

*Dr. Randall Ross*, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Ross is responsible assisting Dr. Wilkin in designing the ground-water sample collection methodology and for assisting in the collection of ground-water samples. His HAZWOPER certification is current.

*Mr. Steven Acree*, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Mr. Acree is responsible assisting Dr. Wilkin in designing the ground-water sample collection methodology and for assisting in the collection of ground-water samples. He is the co - work assignment manager for overseeing the installation of monitoring wells. His COR and HAZWOPER certifications are current.

Dr. Junqi Huang, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Huang is responsible for development of a conceptual model for ground-water flow. His HAZWOPER certification is current.

Ms. Kristie Hargrove, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Ms. Hargrove is responsible for assisting Dr. DiGiulio in collecting soil-gas samples and in maintaining, operating, and calibrating all portable gas analyzers used in the field. Her HAZWOPER certification is current.

Mr. Ken Jewell, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Jewell is responsible for operation of the Geoprobe rig during soil-gas sampling. His HAZWOPER certification is current.

Mr. Russell Neill, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Neill is responsible for operation of the Geoprobe rig and assisting Dr. DiGiulio in overseeing installation of monitoring wells. His HAZWOPER certification is current.

Mr. Tim Lankford, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Lankford is responsible for assisting Mr. Jewell and Mr. Neill in operation of the Geoprobe rig. His HAZWOPER certification is current.

Mr. Tony Lee, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Lee is responsible for assisting in the ground-water sampling. His HAZWOPER certification is current.

Dr. Doug Beak, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Dr. Beak is responsible for assisting in the ground-water sampling. His HAZWOPER certification is current.

Mr. Steve Vandegrift, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Vandegrift is responsible for quality assurance review/approval of the Quality Assurance Project Plan (QAPP), conducting audits, and QA review/approval of the final report. His HAZWOPER certification is current.

Mr. Robert Parker, U.S. Environmental Protection Agency – Region VIII, Denver, CO. Mr. Parker is the CERCLA project manager for the Pavillion investigation and is responsible for overall project coordination between EPA Region VIII and NRMRL-Ada including obtaining access agreements for monitoring well installation and soil-gas sampling. His HAZWOPER certification is current.

Mr. Gregory Oberley, U.S. Environmental Protection Agency – Region VIII, Denver, CO. Mr.

Oberley is responsible for coordinating technical discussion and activities between NRMRL-Ada and EPA Region VIII. His HAZWOPER certification is current.

Mr. Nathan Wiser, U.S. Environmental Protection Agency – Region VIII, Denver, CO. Mr. Wiser is responsible for assisting NRMRL-Ada in selecting locations for ground-water and soil-gas sampling. His HAZWOPER certification is current.

Dr. Sujith Kumar, Shaw Environmental, Ada, OK. Dr. Kumar is responsible for overseeing all contracting and subcontracting of work related to installation of monitoring wells.

Steve Pelphrey, Isotech Laboratories, Inc. Champaign, IL. Mr. Pelphrey is responsible for overseeing the fixed-laboratory analysis of soil-gas samples.

## **2.2 Lines of Communication Among Project Participants**

Dr. DiGiulio is responsible for initiating contact with appropriate project participants as he deems necessary. Other project participants will keep Dr. DiGiulio informed whenever significant developments or changes occur. Lines of communication among project participants may be conducted via in person conversations, electronic mail, phone conversations, conference calls, and periodic meetings.

## **2.3 Specialized Training or Certificates**

HAZWOPER certification is required for on-site work and visits, such as QA audits. Ms. Hargrove is certified to ship "Dangerous Goods" according the U.S. Department of Transportation guidelines and has received training for shipping samples via UPS.

## **2.4 Process and Responsibilities to Ensure Project Participants Have Current QAPP**

Each member of the research team (Dr. Wilkin, Dr. Ross, Dr. Huang, Dr. Beak, Mr. Acree, Mr. Jewell, Ms. Hargrove, Mr. Lankford, Mr. Neill, Mr. Lee) will be provided the most current draft version of the QAPP for comment and will be provided updated versions if the QAPP is modified. The approved QAPP and any subsequent approved revisions shall be provided to those in the Distribution list on cover page. They will typically be distributed electronically via electronic mail. The original QAPP Revision number is "0." Future revisions will be numbered incrementally.

# **3.0 Scientific Approach**

## **3.1 Ground-Water Monitoring**

The ground-water sampling component of this project is intended to provide a survey of water quality in the area of investigation. NRMRL-Ada and EPA Region VIII will survey the area and speak to landowners in late April 2010 to determine the location of monitoring wells. NRMRL-Ada will issue a contract through its on-site contractor, Shaw Inc., to install two deep (e.g., 800'-1000'), designated as *Type A* monitoring wells. Monitoring well installation will occur in June and July 2010. Monitoring wells will be installed in locations where contamination is suspected based on previous sampling of domestic wells by EPA Region VIII. There is a shallower (600') domestic well near the location of a planned deep monitoring well without a pump that is currently not being used that will be sampled. This is designated as a *Type B* monitoring well.

Ground-water samples will also be collected from domestic wells via homeowner taps. These wells are designated as *Type C* wells. Most domestic wells are screened between 200' - 300'. However several domestic well are shallow (e.g., 60') while others are fairly deep (e.g., 750'). It is anticipated that the monitoring wells will be sampled three times over a period of 1 year. The spacing of the ground-water sampling events will in part depend on weather conditions but is anticipated to start in July 2010 and continue in the fall of 2010, and the spring of 2011. The study area and locations of Type A and B monitoring wells are illustrated in **Figure 1**. The latitude, longitude, and elevation of monitoring wells will be recorded.

### 3.2 Soil-Gas Survey

A soil-gas survey using the Geoprobe Post Run Tubing (PRT) System with a retractable probe will be conducted in July 2010. The Geoprobe rig will also be used to install approximately 15 dedicated vapor probes at this time. If the weather is favorable, probing will take place at 40 to 50 locations. Probing will be limited to areas where EPA Region VIII has signed access agreements with landowners. This includes most of the area illustrated in **Figure 1**. Probing on property will commence near potential source areas (e.g., pits and production wells) and then proceed radially outward increasing in distance between probed areas with distance from potential source areas. The latitude and longitude of each measurement location will be recorded.

If soil conditions are favorable (e.g., 5 or more meters of unsaturated unconsolidated deposits) oxygen (O<sub>2</sub>), CO<sub>2</sub>, methane (CH<sub>4</sub>), hydrogen (H<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), and total hydrocarbons will be measured at three depths using portable gas analyzers. Otherwise, soil-gas will be screened at only one or two depths. Gas permeability will also be measured. Upon attainment of maximum penetration depth (40 to 50') or probe refusal whichever comes first, leak testing will be conducted using a chamber, tracers, and portable gas analyzers.

### 3.3 Soil-Gas Sampling

Dedicated soil-gas probes installed in July 2010 will be sampled in September, 2010. Leak, purge, and gas permeability testing will precede collection of each soil-gas sample. A sample will not collected if leakage exceeds 10%, a standard used by the State of New York (2006). Samples will be submitted to Isotech Laboratories for analysis of: (1) fixed gases - argon (Ar), helium (He), H<sub>2</sub>, O<sub>2</sub>, nitrogen (N<sub>2</sub>), CO<sub>2</sub>; (2) hydrocarbons - CH<sub>4</sub>, ethane (C<sub>2</sub>H<sub>6</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), propane (C<sub>3</sub>H<sub>8</sub>), isobutane (iC<sub>4</sub>H<sub>10</sub>), normal butane (C<sub>4</sub>H<sub>10</sub>), isopentane (iC<sub>5</sub>H<sub>12</sub>), normal pentane (nC<sub>5</sub>H<sub>12</sub>), and hexane plus (C<sub>6</sub>+); (3) isotopes - stable isotopes of carbon in CH<sub>4</sub> and CO<sub>2</sub> (δ<sup>13</sup>C), stable isotopes of hydrogen in CH<sub>4</sub> (δD), and radiocarbon isotopes of CH<sub>4</sub> (Δ<sup>14</sup>C). A study will be conducted to evaluate the stability of gas concentrations in Cali-5 Bond sampling bags over a 30 day period. This study will be completed prior to collection of soil-gas samples in September 2010.

#### 3.3.a. Rationale for Soil-Gas Sampling Strategy

In an extensive natural gas and petroleum exploration program carried out by the Gulf Oil Research Center between 1972 and 1983, Jones and Drozd (1983) observed that soil-gas measurements can be used to help locate natural gas and petroleum deposits and that soil-gas anomalies of light hydrocarbons often occur along faults and fractures. They also observed similarity between soil-gas and reservoir gas composition. These two observations indicate that transport of hydrocarbon vapors to the vadose zone and thus also to ground water is dominated

by advection through faults and fractures rather than by diffusion through faults, fractures, and structured geologic media. Their observations are consistent with studies in volcanic or geothermal areas where magma degassing, thermo-metamorphic alteration of carbonates, and advective transport through faults and fractures results in high concentrations of CO<sub>2</sub>, H<sub>2</sub>, He, H<sub>2</sub>S, and radon detected in soil-gas and ground water (Azzaro et al., 1998; Baubron et al., 2002; Ciotoli et al., 2007; Fountain and Jacobi, 2000; King et al., 1996; Lewicki and Brantley, 2000; Lewicki et al., 2003). If gas migration is occurring through faults and fractures and by analogy well penetrations in the Pavillion area, soil-gas sampling may be viable and inexpensive method to detect and locate migration pathways. These observations would then be confirmed with similar detection in ground-water samples.

As illustrated in **Figure 2**, soil-gas anomalies generally occur as linear, fault-linked anomalies, as well as in irregularly shaped diffuse or halo anomalies and irregularly spaced plumes or spot anomalies (Ciotoli et al., 1999). Linear anomalies longer than several meters are commonly taken as strong evidence of gas migration along gas-bearing faults (Fridman, 1990; Ciotoli et al., 1998). Most faulted zones are caused by fault intersections and have extensive associated fractures that allow gases to escape laterally and vertically producing halo or diffuse anomalies (Matthews, 1985). Gas emanation from faults is not always continuous (Ciotoli et al., 1998). Multiple spot anomalies occurring along a linear trend may indicate spatially discontinuous gas conduction (Lombardi et al., 1996; Ciotoli et al., 1998). Gas migration through production or abandoned wells would have a spot anomaly near the surface. The ultimate distribution in constituents in soil gas depends on the permeability of rocks, depth of origin, and the influence of near-surface conditions such as ground-water flow, weathering, etc. (Ciotoli et al., 2004). These observations mean that a soil-gas survey must cover a wide area with subsequent refinement in areas of suspected anomalies. This is the strategy that will be employed at Pavillion.

There are a number of potential limitations to using soil-gas sampling to detect leakage or the potential for leakage of CO<sub>2</sub> during geologic sequestration and hydrocarbons at Pavillion. Prior to injection of CO<sub>2</sub> at a petroleum reservoir for enhanced oil recovery, the reservoir may be underpressurized thereby reducing the driving force for advective transport of hydrocarbons toward the surface. This could limit the use of soil-gas sampling to detect potential migration pathways such as plugged or improperly plugged abandoned wells prior to injection of CO<sub>2</sub>. Thus, if leakage occurs, detection of migration pathways would occur after rather than before injection. Soil-gas and ground-water monitoring may be necessary near plugged abandoned wells because geophysical logging to ensure well integrity is irrelevant in this case. Given the observation of a highly pressurized natural gas blowout during drilling of a domestic well, this limitation is not a factor at Pavillion. Second, spillage of hydrocarbons near petroleum or natural gas wells could complicate data interpretation (source of hydrocarbons and other gases may be from a near surface source). A vertical gas profile especially in thick unconsolidated unsaturated deposits could help resolve this issue. Third, the presence of multiple confining layers and intervening permeable formations would likely greatly diminish leakage from an abandoned well into a USDW or the vadose zone. For the case of single-fluid flow, Norbotten et al. (2004) conducted simulations to show that for a layered system, leakage from an abandoned well that reached the surface was reduced by orders of magnitude compared to the case of a single thick overlying aquitard due to the availability of permeable layers along the vertical column. Nordbotten et al. (2005a,b) derived a semi-analytical solutions to estimate the radial spread of a plume of injected gas around an injection well and conducted similar simulations. The solutions analyzed the extent of the injected CO<sub>2</sub> plume, provided leakage rates through abandoned wells, and estimated the CO<sub>2</sub> plume extent into overlying formations into which the fluid leaks.

LeNeveu (2008) examined the effect of multiple layers on leakage through a borehole and also showed that in the event of a wellbore leak, a significant amount of the carbon dioxide rising in and around wellbores can dissolve into the formation water above the caprock before reaching the biosphere. Thus, while providing a beneficial effect, the presence of multiple confining layers would significantly reduce the signal to noise ratio for detection of leakage from abandoned wells. This may not be an issue at Pavillion because many production wells are relatively shallow (e.g., less than 1500')

Thus, in general, subsurface conditions at Pavillion indicate that soil-gas sampling should be effective in detecting and determining locations of gas migration into underground sources of drinking water. If gas migration is accompanied by chemicals used for enhanced gas production, soil-gas sampling may be useful in locating areas of chemical intrusion. In regard to chemical migration, the usefulness of this approach needs to be confirmed with the observation of organic compounds and geochemical changes in ground water such as pH, total dissolved solids (TDS) (indirectly measured as specific conductance), oxidation-reduction potential, and element concentrations in addition to changes in stable and radiocarbon isotopic ratios.

### 3.2.b Selection of Soil-Gas Monitoring Parameters

The following discussion provides a rationale for selection of gases to analyze during soil-gas sampling.

#### Carbon Dioxide and Oxygen

Depressed levels of O<sub>2</sub> and elevated levels of CO<sub>2</sub> in soil gas can be due to: (1) biodegradation of hydrocarbons from an anthropogenic source (e.g., spillage of petroleum) in the vicinity of measurement, (2) biodegradation of CH<sub>4</sub> and other light hydrocarbons seeping from a petroleum or natural gas reservoir, (3) oxidation of native organic matter in soil, and (4) geochemical reactions in soil and ground water. Since oxidation of organic matter and hydrocarbons is accompanied by reduced O<sub>2</sub> concentration, concentration ratios of CO<sub>2</sub> and O<sub>2</sub> will be used to examine oxidation as a source of CO<sub>2</sub>. Observation of increased CO<sub>2</sub> bulk soil gas concentration with depth would indicate migration from ground water or a deeper source as opposed to oxidation from near surface organic matter.

#### Light Hydrocarbons

Thermogenic light hydrocarbons detected in soil gas typically have a well-defined composition indicative of reservoir composition. The concentration of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and nC<sub>4</sub>H<sub>10</sub> hydrocarbons almost always occur in the following order: CH<sub>4</sub> > C<sub>2</sub>H<sub>6</sub> > C<sub>3</sub>H<sub>8</sub> > nC<sub>4</sub>H<sub>10</sub> (Jones et al., 1999). Methane dominates the light hydrocarbon fraction above natural gas reservoirs whereas significant concentrations of C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and nC<sub>4</sub>H<sub>10</sub> are found in soil gas overlying petroleum reservoirs. Ratios of light hydrocarbons generally plot as CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> < CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> < CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub> < CH<sub>4</sub>/nC<sub>5</sub>H<sub>12</sub> with typical upper limits for dry-gas reservoir ratios of: CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> < 350, CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> < 900, CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub> < 1,500, CH<sub>4</sub>/nC<sub>5</sub>H<sub>12</sub> < 4,500. Biogenic gas and gas from coal bed deposits typically have ratios of CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> that exceed 1000 or 10,000 (Janezic, 1979). Also, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and nC<sub>4</sub>H<sub>10</sub> are not produced by biological processes in near surface sediments (Jones and Pirkle, 2009). Only CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> are products of biodegradation. Thus, elevated levels of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and nC<sub>4</sub>H<sub>10</sub> in soil gas are indicative of thermogenic origin and serve as natural tracers for natural gas migration from a reservoir.



## Hydrogen Sulfide

Hydrogen sulfide is produced during the anaerobic decomposition of organic matter by sulfur bacteria. It is also found in varying amounts in unrefined natural gas and petroleum, in sulfur deposits, volcanic gases and sulfur springs. Thus H<sub>2</sub>S may serve as a natural tracer for natural gas migration.

## Hydrogen and Helium

Because H<sub>2</sub> and He are chemically inert, physically stable, and highly insoluble in water, they are widely recognized as good fault and fracture indicators (Klusman, 1993; Ciotoli et al., 1999; Ciotoli et al., 2004). Helium and H<sub>2</sub> have been observed in soil gas at values up to 430 and 50 ppmv respectively over the San Andreas fault in California (Jones and Pirkle, 1981). Wakita et al. (1978) observed He at a maximum concentration of 350 ppmv along a nitrogen vent in Japan. Wakita et al. (1980) reported hydrogen anomalies ranging from 2 to 30,000 ppmv H<sub>2</sub> along the Yamasaki fault zone in Japan with ambient background values of 0.5 ppmv observed outside the influence of the fault. The atmospheric concentration of helium is 5220 ± 15 ppbv.

The presence of He in soil gas is often independent of the oil and gas deposits. However, since He is more soluble in oil than water, it is frequently found at elevated concentrations in soil gas above natural gas and petroleum reservoirs and hence may serve as a natural tracer for gas migration.

## Carbon and Hydrogen Isotopes

Carbon and hydrogen isotope analysis is very useful in determining the origin of CH<sub>4</sub>, other light hydrocarbons, and CO<sub>2</sub> in soil gas. Isotopes are reported as the relative difference in the ratio of the less abundant heavier isotope to the more abundant lighter isotope of the sample with respect to a reference standard. Ratios are expressed in parts per thousand or permil (‰). Stable carbon isotope analysis of δ<sup>13</sup>C is defined as:

$$\delta^{13}\text{C} \text{ (‰)} = \left( \frac{^{13}\text{C}/^{12}\text{C} \text{ sampled}}{^{13}\text{C}/^{12}\text{C} \text{ standard}} - 1 \right) \times 1000$$

where the standard is the Pee Dee Belemnite (PDB) reference standard. Δ<sup>14</sup>C is defined as:

$$\Delta^{14}\text{C} \text{ (‰)} = \left( \frac{^{14}\text{C}/^{12}\text{C} \text{ sample}}{^{14}\text{C}/^{12}\text{C} \text{ standard}} - 1 \right) \times 1000 .$$

The reference standard is oxalic acid decay corrected to 1950. δD is defined as

$$\delta\text{D} \text{ (‰)} = \left( \frac{^2\text{H}/^1\text{H} \text{ sampled}}{^2\text{H}/^1\text{H} \text{ standard}} - 1 \right) \times 1000$$

where the standard is the Vienna Standard Mean Ocean Water Standard.

Baldassare and Laughrey (1997), Schoell (1980, 1983), Kaplan (1997), Rowe and Muehlenbachs (1999), and others have summarized interpretation of values of  $\delta^{13}\text{C}$  and  $\delta\text{D}$  for  $\text{CH}_4$ . As illustrated in **Figure 3**, it is often possible to distinguish  $\text{CH}_4$  formed from microbial and thermogenic processes by plotting  $\delta^{13}\text{C}$  for  $\text{CH}_4$  versus  $\delta\text{D}$  for  $\text{CH}_4$ . For  $\text{CH}_4$  found in near-surface environments due to acetate fermentation (marsh gas and landfill gas), values of  $\delta^{13}\text{C}$  for  $\text{CH}_4$  range from -40 to -62‰ and values of  $\delta\text{D}$  for  $\text{CH}_4$  range from 270 to -350‰. For outwash deposits, values of  $\delta^{13}\text{C}$  for  $\text{CH}_4$  range from -62 to -90‰ and values of  $\delta\text{D}$  for  $\text{CH}_4$  range from about -180 to -240‰. For  $\text{CH}_4$  of thermogenic origin, values of  $\delta^{13}\text{C}$  for  $\text{CH}_4$  range from -28 to -60‰ and values of  $\delta\text{D}$  for  $\text{CH}_4$  range -110 to -250‰. Values of  $\delta^{13}\text{C}$  for  $\text{CH}_4$  near -60‰ associated with values of  $\delta\text{D}$  for  $\text{CH}_4$  in the -160 to -260‰ range are attributed to mixing of thermogenic and microbial methane.

Since radiocarbon has a half-life of 5730 years, ancient organic matter and fossil fuels such as natural gas are  $^{14}\text{C}$ -free meaning that undiluted thermogenic  $\text{CH}_4$  or  $\text{CO}_2$  from degradation of thermogenic  $\text{CH}_4$  will have a value of  $\Delta^{14}\text{C}$  near -1000‰.

## 4.0 Sampling Procedures

Samples will be retained by the laboratories until the principal investigators give permission for disposal.

### 4.1 Ground-Water Sampling

#### 4.1.a Background Hydrogeological Information

The USGS published a report entitled “*Monitoring-Well Network and Sampling Design for Ground-Water Quality, Wind River Indian Reservation, Wyoming (2005)*” which could be helpful in discerning background hydrogeological conditions. As illustrated in **Figure 4**, hydrostratigraphy in the area can be divided into local Quaternary age aquifers, 10 bedrock aquifers, and 11 confining layers. Quaternary age media include alluvium, colluvium, eolian, terrace, pediment, landslide, glacial, and travertine deposits. Quaternary age deposits are generally less than 50 ft thick yield 2 to 60 gallons per minute (gal/min), and have dissolved-solids concentrations range from 109 to 4,630 milligrams per liter (mg/L). Tertiary age deposits include the Wind River, Fort Union, and Indian Meadows Formations. In the Wind River basin trough, the Wind River and Fort Union have combined thickness in excess of 10,000 ft. However, thickness varies greatly throughout the basin. The Indian Meadows Formation lies between the Wind River and Fort Union Formations, but it is not differentiated in the subsurface of the Wind River Structural Basin. Water yields from wells in the Wind River Formation range from 0.1 to 350 gal/min, and dissolved-solids concentrations range from 211 to 5,110 mg/L. These large ranges result in part from the varied lithology of the formation. Tertiary volcaniclastic rocks of the Wiggins, Tepee Trail, and Aycross Formations occur above the Wind River Formation. Water quality samples collected from springs discharging from volcaniclastic rocks have dissolved-solids concentrations ranging from 197 to 244 mg/L. Discharges from the springs range from 8 to 37 gal/min. At depths of greater than a few thousand feet it is likely that the water from Tertiary aquifers is highly saline (dissolved-solids concentrations between 10,000 and 35,000 mg/L) to briny (dissolved-solids concentrations greater than 35,000 mg/L). Mesozoic rocks consist mostly of siltstone, sandstone, and shale. Smaller amounts of claystone, conglomerate, coal, bentonite, limestone, dolomite, and gypsum also are present. These rocks are overlain by thick Tertiary deposits, except near the flanks of the mountains and around some of the structures in the basin. Water yields from wells in Mesozoic aquifers range

from 0.5 to 90 gal/min, and dissolved-solids concentrations range from 182 to 6,060 mg/L. In general, the median values for dissolved-solids concentrations in the water samples from Mesozoic aquifers are about 1,000 mg/L, except in water samples from the Cody Shale, which has a median value of 2,540 mg/L. It is likely that most of the water samples from Mesozoic aquifers evaluated came from relatively shallow depths near recharge areas. Away from these areas, water from Mesozoic aquifers probably is saline to briny. Paleozoic rocks are composed mostly of sandstone, shale, limestone, and dolomite, with some chert. Well-yield and water-quality records are sparse for Paleozoic aquifers. Dissolved solids in Paleozoic aquifers range from less than 500 mg/L to more than 3,000 mg/L. Most of these water-quality samples probably came from shallow depths (less than a few thousand feet). In the central basin area where these rocks are deeply buried, the dissolved-solids content is probably much greater.

#### 4.1.b Installation of Monitoring Wells

NRMRL-Ada's on-site contractor, Shaw Inc., will be tasked with drilling and installation of two deep monitoring well wells. A local driller, Mr. Louis Dickinson, states that a highly productive white coarse-grained sandstone aquifer exists at 800 - 1000' in this area. The goal of drilling is to place monitoring wells in this deposit which is part of the Wind River Formation. An interview was conducted with Mr. Dickinson, to determine stratigraphy around and within the area of deep monitoring well installation. Domestic wells in the area were drilled with mud rotary. One deep well will be drilled on the Louis Meeks property. In December 2005, Mr. Meeks contracted Mr. Dickinson to drill a domestic well to replace his existing well screened at 210'. Mr. Meeks complained of "petroleum-like" odors and taste associated with the water. While drilling the well, Mr. Dickinson recorded deposit as a function of depth outlined below.

<u>Depth (ft)</u>	<u>Deposit</u>
0 - 15	top soil
15 - 75	brown sandstone
75 - 90	gray coarse-grained sandstone
90 - 140	red and green claystone
170 - 195	gray shale
195 - 210	gray fine-grained sandstone
210 - 445	gray shale
445 - 460	gray fine-grained sandstone
460 - 520	gray shale
520 - 540	gray medium-grained sandstone
540 - 550	gray shale

Mr. Dickinson states that while developing the well to remove drilling mud, a methane gas blowout occurred on 12/19/05. The well was shut-in on 12/22/05. When the well was shut-in, a significant increase in gas production was noted in production well 14-2. Mr. Meeks states that he began smelling gas at 160 - 180' during drilling.

Another deep monitoring well will be located on the Jeff Locker property. Dr. Dickinson installed a deep domestic well in a nearby location and recorded deposit as a function of depth outlined below.

<u>Depth (ft)</u>	<u>Deposit</u>
0 - 70	brown coarse-grained sandstone
70 - 170	gray shale

170 - 205	gray medium-grained sandstone
205 - 245	gray shale
245 - 335	gray medium-grained sandstone
335 - 420	gray shale
420 - 520	gray medium-grained sandstone
520 - 575	gray shale
575 - 595	gray fine-grained sandstone
595 - 840	gray shale
840 - 850	red and green claystone
850 - 875	white coarse-grained sandstone
875 - 940	red claystone
940 - 1000	green claystone
1000 - 1050	white coarse-grained sandstone
1050 - 1060	green claystone

Monitoring well installation will occur in June and July 2010. Drilling and installation of deep wells will require the use of blowout protection (BOP) to ensure the safety of workers and prevent potential loss of commodity (natural gas). BOP is common when drilling in fields containing natural gas.

Shaw Inc. will provide the following tasks to support for drilling and monitoring well installation.

- Explore both the feasibility and cost of drilling deep wells using methods that include roto-sonic, air rotary with casing advance, water rotary, and mud rotary.
- Compile a list of drillers capable of installing deep monitoring wells with BOP. This list does not have to be limited to the State of Wyoming. Since this is a CERCLA investigation, drilling permits are not required.
- Explore the costs associated with continuous coring of deep wells versus coring only screened intervals (20' for deep wells), versus no coring (just cuttings).
- Provide a geologist to log cuttings and/or core material during drilling.
- Provide a cost estimate for open hole logging of one or more deep wells during drilling. The primary purpose of logging is to assist in identification of lithology. Methods to consider include resistivity and density logging.
- Determine well screen and casing materials to ensure a minimum internal diameter of 4 inches. A 20 foot screen will be used for deep wells. The screen will be placed in the white coarse-grained sandstone.
- Survey the location and elevation of casing.
- Dispose of drilling cuttings including muds and drilling fluids as required by State law. Shaw may need to sample and analyze fluids as part of disposal.
- Develop monitoring wells and dispose of purge water as required by State law. Wells will be developed until the following conditions are met:
  - < 10 NTU

- minimum of 3 purge volumes even if < 10 NTU if obtained prior to attainment of 3 purge volumes
  - attainment of at least 5 purge volumes if < 10 NTU is not achieved after 3 purge volumes.
- Ensure that drilling does not occur near buried utility lines. In the event that a buried line is punctured, the Contractor will be responsible for contacting the relevant utility company and repair of a utility line if necessary.

Shaw Inc. will develop a separate QAPP for drilling which will be reviewed independently of this document. Shaw Inc. will report on the completion of all TDs in the form of a letter, memo, or other written correspondence to completely address the particular work request. Such documentation shall be addressed to the PO/WAM. This documentation shall reference the TD number, the method(s) used, and comments on any problems or specifics.

Monitoring wells may be located within 100 feet of an existing production well. Wells however will be located off paved roads and on domestic property where EPA Region VIII has gained access. Expansion or improvement of roads will not be necessary to drill. There are no cultural sites or endangered species to be protected. There are no natural features (e.g., streams) that will need protection.

#### 4.1.c Ground-Water Monitoring

A bomb sampler, (**Figure 5**) will be used to sample water from Type A and Type B monitoring wells in order to insure that representative samples are collected for pressure-sensitive dissolved gas analyses. The bomb sampler will be deployed after wells are purged. The following methodology will be used for all Type A and Type B monitoring wells. Refer to **Figure 6**.

- 1) An Idronaut Ocean Seven 303 CTD Multiparameter Probe will be lowered down the monitoring well using a logging truck. The probe will be positioned approximately at the top of the screened interval of the monitoring well. The multiparameter probe will record geochemical parameters of interest, such as pH, oxidation-reduction potential, specific conductivity, dissolved oxygen concentration, and temperature. As a contingency plan, a Century Geophysical Corporation E-log tool (model number 7044) will be used as a downhole probe to measure and track the stabilization of specific conductance.
- 2) Next, a Proactive Monsoon (stainless steel) pump will be positioned in the monitoring well approximately 20 feet below the ambient ground-water level. Either a portable Honda EM2500 watt generator or a Honda EB5000 watt generator installed on the logging trailer will be used to power the pump. Alternatively, a Grundfos Redi-Flo2 pump with a variable frequency controller will be used to pump ground water. Polyethylene tubing will be used (OD=0.625 inch, ID=0.500 inch). The initial expected pumping rate is 1 L/min. The rate of pumping will be determined by measuring the water volume collected after 30 seconds into a 1 L graduated cylinder and iteratively adjusting the flow; the desirable pumping rate should be  $1 \pm 0.5$  L/min. The pumping rate will be adjusted to maintain minimal drawdown. Therefore, the final pumping rate will depend on the hydraulic conductivity of the formation screened by each well. Drawdown will be manually monitored using a Solinst Model 101 water level indicator before sampling and every hour during sampling. Drawdown will also be recorded using an In-Situ Level Troll

700 pressure transducer/data logger with a 15 psig range set to acquire water level data once per minute.

- 3) Once pumping of ground water is initiated, geochemical parameters acquired with the multiparameter probe or the specific conductance probe will be monitored for stabilization. Geochemical parameters will be used to track and establish when representative formation water is accessed by the downhole probe. In general, the following guidelines will be used to determine when parameters have stabilized: pH changes <0.02 standard units per minute, ORP changes <2 mV per minute, and specific conductance changes <1% per minute. These criteria are initial guidelines, however, professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs.
- 4) Once stabilization occurs, the final values for pH, ORP, specific conductance, dissolved oxygen, and temperature will be recorded. The amount of purge water necessary to achieve stabilization will be calculated by multiplying the total pumping time (min) by the average flow rate achieved (L/min). This volume will be recorded on a well-by-well basis and used for subsequent sampling activities. The downhole probes (Idronaut or Century Geophysical Corporation E-log tool) are designed for use in deep sea or deep subsurface investigations. The probes are designed to provide accurate readouts at high pressure.
- 5) Next the Idronaut multiparameter probe or conductance probe and the pump will be retrieved from the well. The logging trailer will be used to lower the bomb sampler (Century Geophysical Corporation Fluid Sampler, 1 liter, 303 SS, model # 9751 plus 2x 500 mL 304 SS vessels; **Figure 5**) through the well opening and to the desired depth within the screened interval. A double-valve configuration will be used to attach two 500 mL vessels and a 150 mL stainless steel sampling vessel (Swagelok, 150 mL, 304L SS, part #304L-HDF4-50a). This series of sampling vessels will be used to collect ground water in one sampling pass, including pressurized samples for dissolved gas analyses. The pump will again be lowered to the same depth and the volume of water determined to attain stabilization will again be pumped. At that time, the bomb sampler will be activated from the surface and ground water will fill the bomb sampler and attached sample vessels. Next, the pump and sampling apparatus will be pulled from the well.
- 6) Each time the bomb sampler is deployed downhole where duplicate or multiple samples are required, the monitoring wells will be re-purged to assure that representative formation water is acquired in the downhole sampler.

Once at the surface, the 150 mL sample vessel for dissolved gas analysis will be detached. The vessel will be stored on ice and returned to Shaw, NRMRL-Ada's on-site contractor, for fixed-laboratory analysis. Shaw will measure dissolved gases in this sample (carbon dioxide, methane, ethane, propane, butane, and acetylene). For every well sampled, a separate 150 mL vessel will be used. This sample will not be acid preserved; therefore, lack of acid preservation will be noted on sample log-in sheets and on the final analytical report of concentration data.

Pressure-insensitive samples will be collected after first expelling the contents of the 1 L plus two 500 mL vessel bomb sampler into a large plastic beaker. A peristaltic pump (Geopump) will be used pump water from the plastic beaker through teflon-lined polyethylene tubing and through high-capacity groundwater filters into pre-labeled sample bottles. The following samples will be collected and in this particular order:

- 1) 125 mL plastic bottle for metals analysis by ICP-OES for Al, Ag, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, Si, and S; this

sample will also be used for ICP-MS analysis for Cd, As, Cu, Pb, Ni, Se, Hg, and Tl. This sample will be filtered and preserved by adding 5 drops of concentrated  $\text{HNO}_3$  (pH test strips will be used to confirm that the sample pH is <2). Test strips for pH will be used on every sample to insure that a proper preservation pH is attained. This is especially important in case high alkalinity samples are encountered during the ground-water sampling.

- 2) 30 mL amber plastic bottle for LC-ICP-MS analysis of arsenic speciation. This sample will be filtered and preserved with 2 drops of concentrated hydrochloric acid (pH test strips will be used to confirm that the sample pH is <2; see note above regarding use of pH test strips).
- 3) 30 mL clear plastic bottle for CE (capillary electrophoresis) sulfate, chloride, and fluoride. This sample will be filtered, no preservative added.
- 4) 30 mL clear plastic bottle for FIA (flow injection analysis) for nitrate + nitrite and ammonium. This sample will be filtered, sulfuric acid added as preservative.
- 5) 45 mL glass VOA vial in duplicate for analysis of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). This sample will be filtered, no preservative added.
- 6) 100 mL glass bottle for analysis of  $\delta^{13}\text{C}$  of dissolved inorganic carbon. This sample will be filtered, no preservative added. Samples will be shipped to Isotech Laboratories for isotopic analyses.
- 7) 20 mL glass VOA vial for analysis of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of water using IRMS. This sample will be filtered, no preservative added.
- 8) Field measurements will consist of alkalinity, ferrous iron, and dissolved sulfide. Alkalinity will be measured by titrating ground water with 1.6N  $\text{H}_2\text{SO}_4$  to the bromcresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to Standard Method 2320B for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH DR/2010 spectrometer, HACH method 8146, equivalent to Standard Method 3500-Fe B for wastewater). Dissolved sulfide will be measured using the methylene blue colorimetric method (HACH DR/2010 spectrometer; HACH method 8131, equivalent to Standard Method 4500-S $^{2-}$  D for wastewater).
- 9) A 1 L sample will be collected for the Region 8 EPA lab. No preservative will be added to the sample. The sample will be stored on and shipped on ice to the Denver (CO) facility for GC-MS analysis. This sample will not be filtered. Samples bottles will be provided by the Region or they will otherwise advise us on what sampling containers to use.
- 10) Unless noted otherwise above, ground-water samples will be submitted to Shaw, NRMRL-Ada's on-site contractor, and the EPA General Parameters (GP) Laboratory, for fixed-laboratory analysis. Specific samples will be delivered to the Region 8 analytical facility or to Isotech Laboratories for isotopic analyses of dissolved inorganic carbon.
- 11) Depending on results of the dissolved gas analysis from the first trip and based on the discretion of the PIs of this investigation, during subsequent sampling trips a third bomb deployment may be carried out to collect a sample for carbon isotopic analysis of dissolved gases (e.g., methane) by Isotech Laboratories. If this sample is collected, it will be stored in a 1 L amber glass bottle and preserved with benzalkonium chloride (2%).
- 12) A summary of QA/QC requirements from SOPs and ground-water sampling details are provided in **Tables 2 and 3**.

Type C ground-water samples will be collected from selected taps of local homeowners. These samples will not be filtered. Samples will be poured directly into sample containers as noted above with the exception of samples for dissolved gas analyses in which water samples will be

collected into 60 mL glass serum bottles with crimp cap seals. The samples will be collected with no head space. To facilitate comparison of data between Type A, B, and C ground-water samples, these dissolved-gas samples will not be acidified. However, a duplicate sample for dissolved gases will be collected and preserved with trisodium phosphate to allow for comparison. It is understood that samples from deep Type C wells may be subject to degassing as they are pumped to the surface, leading to sample results that are probably not as representative as those taken with the sample bombs. Field measurements will also consist of alkalinity, ferrous iron, and dissolved sulfide. In addition, pH, ORP, specific conductance, dissolved oxygen, and temperature will be measured with a YSI Model 5600 multiparameter probe. Water from the taps will be run until these parameters stabilize following the criteria described in section 3.1. Duplicate samples will be collected at a frequency of one in every 5 taps sampled. Two bottles for each parameter to be measured will be collected at the same time.

#### 4.1.d Ground-Water Sample Collection

As part of this study, techniques are being developed to acquire representative samples from deep ground-water monitoring wells. The method described allows for sampling after the ground water flow regime in the vicinity of the monitoring well stabilizes, as in the standard low-flow sampling technique for minimal drawdown and minimal well disturbance. A downhole water quality indicator device (e.g., pH, specific conductance, ORP, dissolved oxygen) will be used to establish the extraction volume for sample collection. Most samples will be filtered with a high-capacity ground water filter. Samples for metals analysis by ICP-OES and ICP-MS will be collected into 125 mL clear plastic bottles and acidified to pH<2 with nitric acid (Optima). Samples for As and Se speciation will be collected into 30 mL amber plastic bottles and acidified to pH<2 with hydrochloric acid (Optima). Samples for anion analysis will be collected into 30 mL clear plastic bottles. Samples for carbon analysis (concentrations and stable isotope analysis) will be collected into 100 mL glass bottles or 1 L amber plastic bottles. Samples for O and H stable isotope analysis of water will be collected into 20 mL VOA vials. Samples for dissolved gas analysis will be collected into 150 mL stainless steel vessels (Type A and B wells) or 60 mL serum bottles with crimp cap seals (Type C wells).

Holding times for all analyses are specified in **Table 2**. Holding parameters have not been determined by IsoTech for the carbon isotope measurements. This topic is outside of the scope of the current study, so these data will be flagged as qualitative. The minimum concentration of DIC and methane necessary for isotope measurements are 100 mg/L and 1 mg/L, respectively. All samples will be placed on ice immediately after collection and kept chilled until return to the laboratory. Duplicate samples will be collected on an average of every 5 ground-water wells sampled. Duplicates will be handled in an identical manner to the primary ground-water samples; separate bomb samples will be retrieved in order to collect duplicate samples. Every sample for analysis will be collected in duplicate. On every day of ground-water sampling campaigns, a blank sample will be collected using deionized water to evaluate contamination from the sampling equipment. The equipment blank will be deionized water poured into the 1 L bomb sampler, emptied into the plastic beaker, and then pumped into sampling bottles. At the same time a source blank will be prepared by pouring deionized water directly into the sampling bottles.

Multiparameter probes used for the measurement of pH, ORP, specific conductance, and dissolved oxygen will be calibrated or checked in the field prior to use following the recommendations provided by the equipment manufacturers. The pH electrode will be calibrated using pH 7 and 10 buffers. If pH < 7 is encountered, the meter will either be



calibrated with pH 4 buffer, or the pH 4 buffer may be measured and if within  $\pm 0.1$  units, its calibration will be considered acceptable. The ORP electrode will be checked by measuring an ORION ORP standard solution ( $200 \pm 20$  mV). The specific conductance electrode will be checked with a 1413 uS/cm standard solution ( $1413 \text{ uS/cm} \pm 5\%$ ). The dissolved oxygen sensor will be calibrated to 100% atmospheric oxygen saturation. The electrode will be checked by reading a zero-oxygen solution. Performance of the pH probes will be checked at mid-day and the end of each day by measuring and recording the pH of a pH 7 ( $\pm 0.1$  standard units) buffer solution. The other probes shall be checked as well with criteria noted earlier in the paragraph).

Decontamination procedures will be used on the bomb sampler, pump and tubing, and the multiparameter probes. After the completion of sampling activities at a well, the bomb sampler will be given an Alconox scrub and wash, followed by 2 potable water rinses, followed by 1 rinse with distilled water. The pump and tubing used in the well will be cleaned by circulating 2 gallons of Alconox solution through the pump for 5 minutes, followed by a potable water recirculation for 5 minutes, followed by a 5 minute recirculation with distilled water. The multiparameter probe will be rinsed with potable water followed by a rinse with distilled water. Multiple sampling assemblies will be available to minimize the amount of decontamination required, i.e., cleaned vessels will be on-hand in the field. Any pump tubing used with the peristaltic pump for sample filtration will be discarded and replaced for each new well sampled.

#### 4.1.e Ground-Water Sampling Labeling

Each well will be uniquely labeled. Samples collected from each well will include the unique label, the date, the initials of the sampler, and designation of the sample type, e.g., "metals". This information will be recorded onto labeling tape, using water-insoluble ink, affixed to each sample bottle.

#### 4.1.f Ground-Water Sample Packing and Shipping

Samples collected from each well will be placed together in a sealed Ziploc plastic bag. The bags will be placed on ice in coolers. Glass bottles will be packed with bubble wrap to prevent breakage. The coolers will be sent via UPS, overnight, to the appropriate lab with chain of custody forms (see **Figure 7**) and custody seal.

R.S. Kerr Environmental Research Center  
919 Kerr Research Drive  
Ada, OK 74820  
1-580-436-8920  
ATTN: Andrew Greenwood  
(for samples analyzed by both Shaw and EPA General Parameters Laboratory)

Isotech Laboratories, Inc.  
1308 Parkland Court  
Champaign, IL 61821  
1-817-362-4190  
ATTN: Steve Pelphrey

#### 4.2 Soil-Gas Sampling

Prior to conducting the soil-gas survey, EPA Region VIII will contact landowners and prepare

access agreements prior to selection of sampling locations. EPA Region VIII will also contact EnCana, owner of petroleum and natural gas wells, to request the presence of a representative during soil-gas sample location selection to ensure that probing does not occur near buried gas pipelines. Based on discussion with homeowners, NRMRL-Ada personnel will mark off additional areas around homes or on land owned by homeowners that should be avoided during probing. Prior to probing, NRMRL-Ada personnel will contact utility companies to review procedures to follow in the unlikely event that a buried utility line is damaged or severed.

#### 4.2.a Geoprobe Post Run Tubing System (PRT)

An area-wide soil-gas survey will be conducted using the Geoprobe PRT system. A retractable probe and connecting rods will be pushed vertically into the ground until the desired depth is reached. The probe rods will be retracted approximately 6 cm. A metal rod will be used to extend the retractable probe to its full length. The probe creates a 2.5 cm (1") diameter, borehole upon retraction. A PRT adapter with low density polyethylene tubing (0.43 cm x 0.64 cm) will be inserted into the probe rods and turned counterclockwise to engage the adapter threads and an O-ring with the point holder. The tubing will be pulled up lightly to test engagement of the threads. The sample is drawn through the point holder, the adapter, and sample tubing. Since the retraction length is 6 cm (2.25") and the diameter of the retraction tube is 0.95 cm (3/8"), the interval volume of the open portion of the hole is approximated by 25 cm<sup>3</sup>. The point holder adds another 24 cm<sup>3</sup> of internal volume. If 0.47 cm (3/16") internal diameter low density polyethylene tubing is used to connect the PRT adapter, the internal volume of tubing = 0.15 \* length of tubing (cm<sup>3</sup>). The tubing will be replaced after each sample eliminating sample carryover problems and the need to decontaminate the probe rods.

#### 4.2.b Installation of Dedicated Soil-Gas Probes

Prior to probing in a "new" (e.g., different property owner, near bedrock outcrop) area, an exploratory borehole will be cored to determine depth to water and variation of soil texture with depth. To create a borehole, a Geoprobe® rig will be used to push and extract 2.25" O.D. 4' long steel Geoprobe® macrocore (MC) samplers to 3' below the water table surface or refusal whichever comes first. Each sampler will contain a 4' long clear polyvinylchloride (PVC) liner to collect soil cores. A MC core catcher will be used with each liner to avoid loss of soil during retrieval. Each core will be sliced open for manual inspection. Soil texture will be determined using the Natural Resources Conservation Service Guide to Texture by Feel modified from S.J. Thien (1979).

It is expected that the water table will be very shallow (less than 5') in some areas, so soil-gas probes will be constructed using a 5' section of schedule-40 PVC 1" I.D. slotted screen and riser pipe. The screen will be set across the water table. This will allow measurement of depth to the water table prior to gas extraction to avoid extraction of water during soil-gas sampling. The probes will be sealed and locked using commercially available expandable well caps to ensure a gas-tight seal. All casing materials will be connected without use of solvents, glues, or materials which would induce contamination into the wells. O-rings will be placed between sections of riser pipe to ensure that the casing was water- and gas-tight.

The sandpack will extend 0.5' below and 0.5' above the screened interval. A 0.5' layer of bentonite chips will be placed above the sandpack to prevent intrusion of grout into the sandpack. A grout tremie pipe will be used to pump a bentonite slurry to the base of the rod string using a stainless-steel rod and 3/8" tubing to create an impervious watertight bond

between the casing and the undisturbed formation surrounding the casing. The bentonite grout will extend to within 30.5 cm (1') of the surface. Probes will be encased in a 20.3 cm (8") diameter bolted metal box at the surface to protect the probes from surface traffic.

#### 4.2.c Soil-Gas Sample Train

Leak, purge, and gas permeability testing will accompany each soil-gas sample collected from dedicated soil-gas probes for fixed laboratory analysis using a 36 cm (14") diameter 25 cm high (10") stainless-steel chamber designed at GWERD. A photograph of the soil-gas sample train is provided in **Figure 8**. Barbed brass 6.35 mm (1/4") fittings are used to inject and monitor a tracer gas mixture. Masterflex® Viton L/S 6.35 mm internal diameter tubing is used to connect the brass fitting used for injection to a 150-mm Cole-Parmer variable area flow meter (0 – 29 LPM) with a needle valve and to a pressurized canister of tracer gas mixture. Viton tubing is used to direct the tracer gas mixture inside or directly above a borehole or PRT tubing to maximize and monitor tracer concentration at potential location(s) of leakage during leak testing. Viton tubing is used to connect the other brass fitting to a portable gas analyzer for monitoring of tracer concentration inside the chamber at the point of injection.

There are four sampling ports on the chamber to allow gas extraction at a screened interval while monitoring and/or introducing tracers in three other screened intervals if desired. Two sample ports consist of stainless-steel Swagelok® quick connect bodies on the exterior and interior of the chamber. One sample port consists of a Swagelok® stainless-steel tee with a stainless-steel Swagelok® quick connect body on the interior of the chamber and two stainless-steel Swagelok® quick connect bodies on the exterior of the chamber. The centrally located port is equipped with a stainless-steel Swagelok® cross with a stainless-steel Swagelok® quick connect body on the interior of the chamber, two stainless-steel Swagelok® quick connect bodies on the exterior of the chamber, and a stainless-steel Swagelok® toggle valve which is then connected to another stainless-steel Swagelok® quick connect body. The configuration of the centrally located sample port allows for collection of samples in evacuated canisters (not used in this investigation) and placement of an inline 1.0 µm polypropylene Whatman disposable filter for gas-water separation. Use of disposable filters eliminates the need to clean the gas-water separator in the event of water entrapment. The toggle valve allows the portion of the sample train upstream from the valve to be shut-in when sampling using evacuated canisters. Stainless-steel Swagelok® single-end shutoff stem (SESO) are used to connect the port used for sampling (two external quick-connects) to the centrally located port. SESO stems remain open when uncoupled.

The toggle valve is connected to Swagelok® 6.35 mm stainless-steel flexible tubing, a stainless-steel Swagelok® barbed fitting, and 6.35 mm (1/4") Tygon Masterflex tubing. The Tygon tubing is feed into a Masterflex E/S Portable peristaltic pump which allows gas extraction at approximately 1 liter per minute (LPM). The tubing is then attached to Nafion® tubing to reduce the relative humidity of the gas stream and to ensure a condensing atmosphere in portable gas analyzers. If the relative humidity of atmospheric air is low (e.g, less than 50%), a Perm Pure moisture exchanger (exchanges water with atmospheric air) will be used. If relative humidity is high (e.g., greater than 50%), a 48" DurrIDGE® Drystik (allows gas flow through an inner tube while removing water vapor via counter flow through an outer tube) will be used. Ambient air will be passed through a cylinder of Drierite and fed to the Drystik to flush water vapor from the tubing. Nafion® is a copolymer of perfluoro-3,6-dioxo-4-methyl-7-octene-sulfonic acid and tetrafluoroethylene (Teflon®). Only three compounds or classes of compounds are normally removed directly by Nafion® tubes: water (H-OH), ammonia (when water is present, NH<sub>3</sub> reacts

to form  $\text{NH}_3\text{-OH}$ ), and alcohols ( $\text{R-OH}$ , where R is any organic group). Thus, Nafion® tubing should not affect gas screening or laboratory analysis. Nevertheless, both standards and equipment blanks will be run through the Nafion® tubing to ensure that this is the case.

Tygon Masterflex tubing will be used to connect Nafion® tubing to a 6.35 mm brass barb and the inlet of a 150 mm Gilmont Accucal flowmeter. Flow is measured in standard cubic centimeters per minute (sccm). The outlet of the flowmeter is connected to a stainless-steel Swagelok® cross equipped with two stainless-steel Swagelok® quick-connect bodies to allow duplicate collection of soil-gas samples in Cali-5 Bond gas sample bags for submittal to Isotech Laboratories. The cross is connected to a stainless-steel Swagelok® toggle valve to allow gas flow through the flowmeter to be shut-in while bypass gas flow from the leak chamber flows through another in line stainless-steel Swagelok® toggle valve in route to portable gas analyzers. This toggle valve allows the use of one gas analyzer to measure gas tracer concentration in the sample train and chamber during leak testing.

A 6.35 mm brass barb on the flowmeter is used to connect the sample train to a GEM2000 Plus CES LandTec Gas Analyzer for continuous measurement of  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{H}_2\text{S}$  in the gas stream for purge testing and screening of soil-gas samples. The outlet of GEM2000 Plus LandTec Gas Analyzer is then fed into a Thermo Scientific TVA-1000B flame ionization detector (FID)/photoionization detector (PID) for continuous measurement of hydrocarbons.

Gas extraction occurs by connecting the quick-connect body on the inside of the chamber associated with the port containing two external quick-connect bodies to the quick-connect body of a soil-gas probe using a stainless-steel Swagelok® double-end shutoff (DESO) stem, Swagelok® 6.35 mm stainless-steel flexible tubing, and a 316 stainless-steel tube-fitting single-end shutoff stem (SESO). A DESO stem has a valve that seals when uncoupled allowing vacuum testing of the entire sample train.

The stainless-steel chamber used for leak testing with dedicated vapor probes will allow approximately 20 cm clearance from the ground surface for soil-gas sampling using the PRT system. Another chamber will be constructed to increase ground clearance to 60 cm. In this case, ports for additional probes in a cluster will not be necessary since there is only one probe per location.

#### 4.2.d Leak Testing

During soil-gas sampling, ambient air may enter a sampling vessel through loose fittings in above ground components of the sampling train or through openings or cracks in and/or around concrete and bentonite seals used to isolate one or more screened intervals at discrete depths. Components of the above ground sampling train will be tested for leakage prior to soil-gas sampling by observing vacuum loss as a function of time. The Ideal Gas Law will be used to estimate flow of ambient air into above ground components of a sampling train as a function of vacuum. A peristaltic pump will be used to create a vacuum of greater than 90 kPa (atmospheric pressure = 101.325 kPa). Vacuum will be measured using a Sper Scientific manometer. Pressure readings will be stored in a PC using a RS232 cable and software provided by the manufacturer. Pressure will be recorded every second. Previous testing using the sampling train indicates that leakage in above ground components is well below 0.1 sccm. Given that sample flow varies from 300 to 1000 sccm, this contribution to overall leakage is negligible.

Evaluation of leakage in a borehole necessitates the use of non-degradable, non-reactive, and relatively conservative (little retention in soil or water) gases with low ambient and subsurface concentration that can be analyzed in real time in the field using portable gas analyzers. Helium, which has a dimensionless Henry's Law Constant (measured as air concentration/water concentration) of 110 at 20°C, is the most commonly used tracer for leak testing. However, He cannot be used in this investigation since it is a target analyte. Carbon monoxide (CO) is a suitable second choice since it is still relatively insoluble in water having a dimensionless Henry's Law constant of 43. For comparison, N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> which is slightly soluble in water have dimensionless Henry's Law Constants of 61, 31, and 1.2 respectively. Soil-gas will be analyzed prior to tracer testing to check for background. If CO is detected at elevated background concentrations in soil-gas, 1,1-dichloro-2,2,2-trifluoroethane (R-123), which has a dimensionless Henry's Law Constant of 1.4, will be used for leak testing. Sulfur hexafluoride is the most commonly used halocarbon for leak testing but its use in this investigation was deemed inappropriate since it has an extremely high global warming potential of 10,000. R-123 has a global warming potential of only 90 (CO<sub>2</sub> = 1.0) and an ozone depletion factor of only 0.02 (R-11 = 1.0).

Tracer gas, CO, at 18,000 ppmv, will be injected into the chamber during leak testing. The flow rate will be measured using a variable area flowmeter. Leak testing of CO at a concentration of 18,000 ppmv and detection at 10 ppmv provides leak detection sensitivity at 0.055%. Leak testing at a concentration of 10,100 ppmv and detection at 25 ppmv provides leak detection sensitivity at 0.25%.

#### 4.2.e Purge Testing

Tubing connected to an initially closed valve at the top of a dedicated vapor probe will have had direct contact with ambient air prior to sampling. Thus, some volume of gas must be extracted prior to sampling to eliminate the influence of ambient conditions. A simple mass balance equation can be utilized to demonstrate that when the initial concentration in a probe is zero, the most conservative condition, extraction of 3 to 5 internal volumes ensures that vapor concentrations entering a sampling vessel are 95% to greater than 99%, respectively, of gas concentrations in the surrounding soils. However, the process of borehole creation and subsequent vapor probe installation likely perturbs vapor concentration some distance from a borehole. Thus, if vapor equilibration has not occurred prior to sampling, greater than 3 to 5 internal volume exchanges (including the internal volume of the sandpack) may be necessary to achieve a stable concentration. This has been observed during an ongoing investigation at another site.

Borehole installation methods such as air rotary, would be expected to impact vapor concentrations a significant distance from a borehole. Air rotary is often used in consolidated media. Rotosonic drilling is frequently used for borehole creation in glacial till where large cobbles are present and in semi-consolidated media and induces intense vibration and heating of soils adjacent to the casing. Direct-push sampling methods such as the Geoprobe PRT system used in this investigation likely results in the least disturbance since sampling is accomplished without removal of soil. However, direct-push techniques compress surrounding soil and may result in air restriction in plastic clayey soils. This has been observed during an ongoing investigation at another site.

A practical approach to evaluating nonequilibrium is to collect sequential samples or samples preceded by various extraction volumes (i.e. purging) until relative stability of vapor

concentration is achieved. During soil-gas sampling, mass removed in the vicinity of a probe is replaced by mass drawn in by gas advection from surrounding soil and by partitioning from soil to water and water to air. If vapor nonequilibrium exists, vapor concentration will increase with gas extraction volume as less contaminated disturbed soil gas is replaced by more contaminated less disturbed soil gas. Subsequent purging efforts then should result in achievement of steady-state concentrations at less purge volumes. This has been observed during an ongoing investigation at another site.

When evaluating the potential impact of excessive purging, concentration reduction during gas extraction will not occur until significant mass removal occurs at and above a probe as relatively clean atmospheric air replaces contaminated soil gas or when the rate-limited mass exchange occurs from high pore-gas velocities. Thus, attainment of a near constant concentration ( $\pm 1\%$  of  $O_2$ ,  $CO_2$ , and  $CH_4$  readings) during purging ensures attainment of equilibrium and the absence of excessive purging. For instance, DiGiulio et al. (2006b) evaluated the effect of extracting a large volume of air from a relatively shallow vapor probe (screened interval 2.1 meters to 2.4 meters below grade). The internal volume of the probe was one liter. The probe had been sealed for at least three months prior to sampling. A total of 103 liters of air were extracted during this test. After the first internal exchange, sample concentration then remained relatively constant.

Readings will be recorded manually onto a spreadsheet illustrated in **Figure 9** and then input into an EXCEL spreadsheet.

#### 4.2.f Gas Permeability Testing

Gas permeability determination is necessary to simulate gas flow in soil during soil-gas sampling. Gas flow modeling is useful in evaluating the volume from which gas is extracted during purging and sampling and the potential for interaction with atmospheric air. This analysis becomes critical when sampling at shallow (e.g., < 1 meter) depths.

There are a number of publications describing field-scale gas permeability tests. These tests however typically involve extraction or injection from a gas well or probe at flow rates exceeding 30 LPM with measurement of pressure in nearby probes. Estimates of radial and vertical permeability represent integrated values over the field of measurement. During soil-gas sampling, gas permeability testing is conducted at much lower flow rates (e.g., < 1 LPM) with measurement of pressure at point of extraction or injection (i.e., single-interval testing). Single-interval testing provides permeability estimation over a relatively small volume of subsurface media thereby providing a mechanism for assessing physical heterogeneity or spatial variability in permeability on a scale much smaller than full field-scale tests.

In highly permeable media such as sand, steady-state conditions are typically achieved in seconds. In silt or media of less permeability, steady-state is typically achieved in tens of minutes. In low permeability media, transient gas permeability testing eliminates the need to wait for attainment of steady state and allows estimation of gas-filled porosity in a formation.

Line-source/sink analytical solutions are commonly used transient gas flow analysis and parameter estimation. The implicit assumption in use of these solutions is that borehole storage effects are insignificant. Varadhan and DiGiulio (unpublished) derived an analytical solution for two-dimensional axisymmetric anisotropic transient gas flow from a well having a finite radius and borehole storage. The analytical solution is described by DiGiulio and Varadhan (2001).

DiGiulio and Varadhan (2001) compared the line-source/sink and finite-radius solutions at the radius of the sandpack during air injection. The line-source/sink solution simulated a more rapid rise in normalized (observed pressure/initial pressure) pressure at early time and a lower normalized pressure at late time compared to the finite-radius solution. The former effect is due to a delayed response from borehole storage. The latter effect is due to simulation at some distance in the formation itself for the line-source/sink solution compared to simulation at the sandpack -formation boundary for the finite-radius solution. Thus, neglecting borehole storage can result in a source of error in estimating gas permeability when conducting single-interval tests.

In this investigation, the analytical solution developed by Varadhan and DiGiulio (unpublished) will be used to interpret single-interval transient gas permeability tests. Pressure readings will be recorded every second using a Sper Scientific manometer and stored in a PC using a RS-232 cable and software provided by the manufacturer. Pressure measurement will occur prior to entry into the gas/water separator to avoid measurement of head loss associated with most above ground fittings. Head loss associated with tubing and quick-connects prior to the point of pressure measurement will be determined at flow rates used for testing and subtracted from pressure differential readings used for analysis. A Gilmont 150 mm variable area Accual flowmeter with a range of 0 to 2100 sccm and a needle valve to control flow will be used to measure flow. The accuracy and precision of the flowmeter is 2% and 1% respectively.

#### 4.2.g Cali-5 Bond Sample Bag Study

A defined holding time is not known for the Cali-5 Bond sample bags. Non-published internal data provided by Isotech Laboratories suggests stability in excess of 105 days for many of the target analytes. However, neither hydrogen nor helium were included, which may be more apt to be lost by diffusion. Attempts to locate published data on holding times for these sample bags was unsuccessful. Isotech Laboratories shall be contracted to conduct this study. To ensure data are not compromised or to identify data that may have been affected by holding times, a study will be done to identify holding times for the target analytes in the Cali-5 Bond sample bags. This study will be done prior to sample collection. If it is determined that gas data may be compromised by exceeding the holding time determined in this study, such data shall be identified with appropriate qualifiers.

Soil-gas samples will be collected in 0.5 liter Cali-5-Bond® evacuated gas sample bags equipped with a Leur-Fit Valve™. A Leur-taper Quick-Mate™ connector with a 4 mm barb fitting will be used to connect flexible tubing to the sampling bag. Cali-5-bond™ gas sampling bags are constructed from inert 5.5 mil thick material made from five layers of film. The layers are comprised of an inner layer of high-density polyethylene, followed by polyamide, an aluminum foil barrier, a polyvinylidene chloride layer and an outer layer of polyester.

The stability of fixed gases, hydrocarbons, and stable isotopes in 0.5 liter Cali-5 Bond gas sampling bags equipped with a Leur-Fit Valve™ will be evaluated. Gas from two standards (low and high concentration) prepared by Isotech Laboratories with the same suite of gases to be analyzed for will be analyzed at 0, 1, 3, 10, 15, and 30 days after sample collection. Gas samples will be analyzed for Ar, He, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, iC<sub>4</sub>H<sub>10</sub>, nC<sub>4</sub>H<sub>10</sub>, iC<sub>5</sub>H<sub>12</sub>, nC<sub>5</sub>H<sub>12</sub>, C<sub>6</sub>+, δ<sup>13</sup>C and δD of CH<sub>4</sub> and δ<sup>13</sup>C for CO<sub>2</sub>. Measurement at time zero will be necessary if components such as H<sub>2</sub> or He are added to an existing standard. A duplicate sample will be collected at each sample period (once every two samples) alternating between high and low standard concentrations. For instance, at time zero, two samples will be

analyzed for the high standard concentration and one sample will be analyzed at the low standard concentration. At time 1 day, two samples will be analyzed for the low standard concentration and one sample will be analyzed at the high standard concentration and so on. This will result in analysis of 18 samples.

The laboratory conducting this work must have demonstrated proficiency in conducting analyses for the determination of concentrations of gas components and stable isotope analyses of carbon in methane and carbon dioxide. This may be demonstrated by accreditation through a recognized authority, such as ISO (International Organization for Standardization), and/or by providing documentation of successful analyses of reference standards. The laboratory shall provide documentation for their QA program (e.g., Quality Management Plan or Quality Assurance Plan).

Fixed gases and hydrocarbons shall be analyzed by gas chromatography and a combination of TCD/FID detectors using a method based upon ASTM D1945-03. Sample reporting units may be mol% or ppmv. Those samples with sufficient concentrations of methane and carbon dioxide (~0.5%) will be analyzed for  $\delta^{13}\text{C}$  of methane and carbon dioxide by isotope ratio mass spectrometry. Method documentation with QC acceptance criteria shall be provided by the laboratory.

Primary standards for  $\delta^{13}\text{C}$  analyses will originate from the International Atomic Energy Agency, Vienna, Austria, and certified by National Institute of Standards and Technology (NIST). Secondary and working standards will be calibrated against the primary standards. Standards for the gas component analysis shall be certified and traceable to NIST.

Accuracy and precision of stable carbon and hydrogen isotope analyses will be within 0.5 per mil or less  $\delta^{13}\text{C}$  and  $\delta\text{D}$ , i.e., the measured value of check or reference standards compared to their known or certified value, and the difference between duplicate sample analysis shall meet this criteria. As previously indicated, every second analysis shall be a sample duplicate. Check or reference standards shall be analyzed every tenth analysis, ensuring that sample runs are always bracketed by standards. Blanks shall be analyzed prior to samples to determine presence of background. Presence of background that would interfere with sample analysis shall be corrected prior to sample analysis.

Accuracy of gas component analysis will be within +/-15%, i.e., the measured value of standards compared to their known or certified value. Precision of the analyses shall be determined by duplicate sample analysis with a Relative Percent Difference (RPD)\* not to exceed 15%. As previously indicated, every second analysis shall be a sample duplicate. Check or reference standards shall be analyzed every tenth analysis, ensuring that sample runs are always bracketed by standards. Blanks shall be analyzed prior to samples to determine presence of background. Presence of background that would interfere with sample analysis shall be corrected prior to sample analysis.

Full data packages shall be provided on CD for all sample analyses to allow for reconstruction of analysis: Chain-of-custody forms, calibration documentation, QA/QC results, raw data, data reduction, data qualifiers, quantitation and detection limits, deviations from method requirements, deviations from QC acceptance criteria, and these deviations' impact to reported results.



$$*RPD = \frac{2(a - b)}{a + b} \times 100$$

Where  $a$  = sample measurement  
 $b$  = duplicate sample measurement ( $a > b$ )

#### 4.2 h Soil-Gas Sample Labeling

Labeling tape will be affixed to each Cali-5 Bond sample bag. Water insoluble ink will be used to record sample identification, date and time of collection, and initials of person collecting the sample on each label.

#### 4.2i Soil-Gas Sample Packing and Shipping

Isotech Laboratories will provide UN approved one gallon metal cans for shipment of Cali-5 Bond sample bags. Up to three 0.5 liter 6" x 8" bags can fit into each can when properly filled. Care will be taken to not compress the sample bags while packing. After packing, the lid will be placed on top of the can sealed by pounding on a plastic ring provided with the can. Metal cans will be placed in fiberboard boxes provided by Isotech Laboratories according to the general instructions included with the box. Samples will be shipped overnight through UPS. If soil-gas samples contain less than 5% methane (or other hydrocarbons), they are not considered flammable nor hazardous for shipping purposes. The Chain of Custody form that will accompany soil-gas samples is illustrated in **Figure 10**.

If samples contain greater than 5% methane, they are considered flammable and require additional labeling and handling. UPS will only accept "Dangerous Goods" from the U.S. Department of Transportation (DOT) certified shippers who have contract with UPS. NRMRL-Ada meets both of these requirements. Isotech Laboratories provides instructions on labeling and shipping boxes containing flammable soil-gas samples which are based on the IATA Dangerous Goods Regulations 48th Edition, 2007". The following labels will be affixed to the outside of the box all on the same side: (1) FLAMMABLE GAS, (2) UN3167, and (3) DANGER DO NOT LOAD IN PASSENGER AIRCRAFT. Labels will not be folded or affixed in such a manner that parts of the same label appear on different faces of the package. A "SHIPPER'S DECLARATION FOR DANGEROUS GOODS" obtained from UPS will accompany soil-gas samples. The information that may be needed on this form is given below.

Proper Shipping Name: Gas Samples, non-pressurized, flammable, n.o.s. (Natural Gas)  
 Class or Division: 2.1  
 UN or ID Number: UN3167  
 Subsidiary Risk: None (leave blank)  
 Packaging Group: None (leave blank)  
 Quantity & Type of Packaging:  
 # Fiberboard boxes box X 4L  
 Packing Instructions: 206  
 Shipment Type: Non-Radioactive  
 Prepared per: ICAO/IATA  
 Additional Information:  
 NRMRL-Ada emergency response telephone number  
 Limitations: Cargo Aircraft Only

As required by the Department of Transportation (49 CFR - Part 172, Subpart G, §172.604) a person who offers a hazardous material for transportation must provide an emergency response telephone number, including the area code or international access code, for use in the event of an emergency involving the hazardous material. A Materials Safety Data Sheet (MSDS), illustrated **Figure 11**, will accompany soil-gas samples exceeding 5% methane.

## 5.0 MEASUREMENT PROCEDURES

### 5.1 Ground Water

Ground-water samples will be collected and analyzed using standard operating procedures. Analysis includes inductively coupled plasma – optical emission spectroscopy (ICP-OES; for cations), inductively coupled plasma – mass spectroscopy (ICP-MS; for trace metals), liquid chromatography - inductively coupled plasma – mass spectroscopy (LC-ICP-MS; for arsenic speciation), capillary electrophoresis (CE, anions), carbon analysis using infrared detection, isotope ratio mass spectroscopy for isotope ratios in water, and gas chromatography (GC, for dissolved gas analysis). These analytical methods and accompanying QA/QC practices (e.g., blanks, calibration checks, duplicates, second source standards, matrix spikes) are described in various in-house Standard Operating Procedures RSKSOP-102v5, RSKSOP-213v4, RSKSOP-175v4, RSKSOP-194v4, RSKSOP-214v5, RSKSOP-257v2, RSKSOP-276v3, RSKSOP-296v0, and RSKSOP-298v0). Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results. An updated version RSKSOP-174v4 will need to be developed by Shaw as part of this study for samples collected from deep wells with the sample bombs. The updated SOP will address analysis procedures for pressurized samples and procedures for carrying out calculations.

Samples will be submitted to Isotech Laboratories for analysis of stable isotope ratios ( $\delta^{13}\text{C}$ ) of dissolved inorganic carbon by gas-stripping and IRMS. A general discussion of QA/QC for Isotech Laboratories is provided in their QAP attached in **Appendix A**. However, acceptance criteria are not included. An inquiry will be made of Isotech for this information.

Samples will be submitted to the Region 8 analytical laboratory for analysis of organic compounds. The resulting data will not be included in this project. Region VIII is responsible for QA/QC for these samples.

### 5.2 Soil-Gas

#### 5.2.a Field Screening During Soil-Gas Survey

A summary of instruments to be used in this investigation, method of measurement (standard operating procedures), concentration range of measurement, concentrations for calibration, and concentrations of gas standards to be used to check the accuracy of instruments is summarized in **Table 4**. The methods to be used are listed in **Table 5**. The accuracy of the instruments will be checked using criteria listed in **Table 5** from the SOPS cited in this table. Gas standards for calibration will be introduced into five-liter SKC Flex Foil sampling bags and feed directly to portable gas analyzers. Check standards will be introduced into ten-liter SKC Flex Foil sampling bags and feed into the sampling train to ensure the absence of flow and material (e.g., tubing, filters, etc) effects.

The Thermo Scientific TVA-1000B will be calibrated at all concentrations listed. Other portable gas analyzers will be calibrated at the concentration specified or at a concentration closest to expected soil-gas concentration. Calibration will occur at the beginning of each work day and when deviation from a check standard at the calibration concentration(s) at the relevant accuracy occurs. The concentration selected for calibration will be that closest to the expected soil-gas concentration. A check standard at the calibration concentration and a method blank will be measured prior to and at the end each sample event and at all concentrations during calibration. "Accuracy" in **Table 4** is per the manufacturer's specifications and may not reflect project requirements.

Carbon monoxide (tracer) will be supplied using gas cylinders (103 liter) obtained from Air Liquide in Plumsteadville, PA using certified gas mixture concentrations with balance air. R-123 (alternative tracer) will be supplied using gas cylinders (221 liter) obtained from Air Liquide America Specialty Gases, LLC from Plumsteadville, PA using certified gas mixtures with balance argon. Two gas standards (103 liter cylinders): (1) 2.5% CH<sub>4</sub>, 5% CO<sub>2</sub>, 10% O<sub>2</sub>, balance N<sub>2</sub> and (2) 2.5% CH<sub>4</sub>, 20% CO<sub>2</sub>, 10% O<sub>2</sub>, balance N<sub>2</sub> will be obtained from Ideal Gas Inc. in Southgate, MI and two gas standards (103 liter cylinders): (1) 50% CH<sub>4</sub>, 35% CO<sub>2</sub>, balance N<sub>2</sub> and (2) 4% O<sub>2</sub>, balance N<sub>2</sub> obtained from James Supply and Rental in Ada, Oklahoma will be used for calibration and concentration checks for O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>. Gas standards for H<sub>2</sub>S and H<sub>2</sub> will be obtained from CES-LANDTEC from Colton, CA.

Carbon dioxide and CH<sub>4</sub> are measured in the GEM2000 Plus using IRGAs. The CO<sub>2</sub> reading is filtered to an infrared absorption frequency of 4.29 μm (nominal), the frequency specific to CO<sub>2</sub>. Therefore, other gases typically detected in soil gas will not affect the CO<sub>2</sub> reading. The CH<sub>4</sub> reading is filtered to an infrared absorption frequency of 3.41 μm (nominal), the frequency specific to hydrocarbon bonds. The presence of other light hydrocarbons (e.g. ethane, propane, butane) will result in a higher reading of CH<sub>4</sub> than actually present. Oxygen, H<sub>2</sub>S, and CO are measured in the GEM2000 Plus using internal electrochemical cells. The O<sub>2</sub> sensor is a galvanic cell type with no influence from CO<sub>2</sub>, CO, H<sub>2</sub>S, SO<sub>2</sub> or H<sub>2</sub>. The electrochemical cell for CO is susceptible to interference from H<sub>2</sub> and H<sub>2</sub>S giving an artificially high reading of CO in the presence of these gases. The GEM2000 Plus uses a 'hydrogen compensated' CO cell to counteract the interference of H<sub>2</sub> and an internal H<sub>2</sub>S filter to eliminate H<sub>2</sub>S cross gas interference.

A Thermo Scientific TVA-1000B will be used to screen for total hydrocarbons using a portable flame ionization detector (FID) and photo ionization detector (PID) according to RSKSOP-320v0 - *Determination of Organic and Inorganic Vapors using the TVA-1000B Toxic Vapor Analyzer*.

#### 5.2.b Fixed-Laboratory Analysis of Soil Gas

Fixed-laboratory analysis of soil-gas samples will be performed by Isotech Laboratories. Approximately 20 soil-gas samples including duplicates, travel, and equipment blanks will be collected from dedicated soil-gas probes in September 2010. All samples and duplicates will be analyzed for Ar, He, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, iC<sub>4</sub>H<sub>10</sub>, nC<sub>4</sub>H<sub>10</sub>, iC<sub>5</sub>H<sub>12</sub>, nC<sub>5</sub>H<sub>12</sub>, C<sub>6</sub>+, δ<sup>13</sup>C and δD of CH<sub>4</sub> and δ<sup>13</sup>C for CO<sub>2</sub>. Equipment and travel blanks will be analyzed for fixed gases and hydrocarbons only. Approximately 15 soil-gas samples will be collected from dedicated vapor probes in September 2010 and analyzed for the components outlined above in addition to Δ<sup>14</sup>C for CH<sub>4</sub>. A Chain of Custody form, illustrated in **Figure 10** will accompany each sample. With the exception of Δ<sup>14</sup>C, turnaround time should be less than

10 days or less from date of sampling.

Fixed gases and hydrocarbons will be analyzed by gas chromatography and a combination of TCD/FID detectors using method based on ASTM D1945-03. Sample reporting units may be mol% or ppmv. Those samples with sufficient concentrations of methane and carbon dioxide (~0.5%) will be analyzed for  $\delta^{13}\text{C}$  of methane and carbon dioxide by isotope ratio mass spectrometry. Samples for determination of  $\Delta^{14}\text{C}$  in methane will be analyzed by accelerator mass spectrometry.

## **6.0 Quality Metrics (QA/QC Checks)**

### **6.1 Quality Metrics (QA/QC Checks) for Field Screening Gas Analysis**

QA/QC requirements for field screening of gas samples are provided in **Table 5**.

### **6.2 Quality Metrics for Fixed Laboratory Gas Analysis**

QA/QC requirements for fixed laboratory analysis of gas samples are provided in **Table 6**.

A summary of field-based QC samples, purpose, method, and frequency for soil-gas sampling is provided in **Table 7**. This is exclusive of QC samples required at Isotech Laboratories.

The laboratory conducting gas analysis must have demonstrated proficiency in conducting analyses for the determination of concentrations of gas components and stable isotope analyses of carbon in methane and carbon dioxide. This may be demonstrated by accreditation through a recognized authority, such as ISO (International Organization for Standardization), and/or by providing documentation of successful analyses of reference standards. The laboratory shall provide documentation for their QA program (e.g., Quality Management Plan or Quality Assurance Plan).

The laboratory will be subject to a QA audit in conjunction with sample analysis or prior to their receipt. Arrangements will be made with the laboratory in advance. Method documentation with QC acceptance criteria shall be provided by the laboratory.

Primary standards for  $\delta^{13}\text{C}$  and  $\delta\text{D}$  analyses shall originate from the International Atomic Energy Agency, Vienna, Austria, and certified by National Institute of Standards and Technology (NIST). Secondary and working standards shall be calibrated against the primary standards. Standards for the gas component analysis shall be certified and traceable to NIST. Standards for  $\Delta^{14}\text{C}$  analysis will be certified and traceable to NIST. Instruments will be calibrated or confirmed to be calibrated prior to sample analysis. Calibration will be linear within the range of use. Initial calibration will be verified by using a second source standard (standard from source different than those used for initial calibration).

Accuracy and precision of stable carbon and hydrogen isotope analyses will be within 0.5 per mil or less  $\delta^{13}\text{C}$  and  $\delta\text{D}$ , i.e., the measured value of check or reference standards compared to their known or certified value, and the difference between duplicate sample analysis shall meet this criteria. At least every tenth analysis will be a sample duplicate\*. Check or reference standards will be analyzed every tenth analysis, ensuring that sample runs are always bracketed by standards. Blanks shall be analyzed prior to samples to determine presence of background. Presence of background that would interfere with sample analysis shall be

corrected prior to sample analysis.

Accuracy and precision of  $^{14}\text{C}$  analysis will be within 1pMC (percent modern carbon). Analysis should be capable of detection to 2.0 pMC with a precision of  $\pm 5\%$ . Standards of known and documented uncertainty will be analyzed at a frequency according to the laboratory's QA requirements and acceptance limits, such that sample runs are bracketed by standards. Blanks will be analyzed prior to samples to determine presence of background. Presence of background that would interfere with sample analysis will be corrected prior to sample analysis.

Accuracy of gas component analysis shall be within  $\pm 15\%$ , i.e., the measured value of standards compared to their known or certified value. Precision of the analyses shall be determined by duplicate sample analysis with a Relative Percent Difference (RPD) defined as

$$RPD = \frac{2|a - b|}{a + b} 100$$

where  $a$  = sample measurement and  $b$  = duplicate sample measurement. RPD should not to exceed 15%. At least every tenth analysis shall be a sample duplicate. Check or reference standards shall be analyzed every tenth analysis. Blanks shall be analyzed prior to samples to determine presence of background. Presence of background that would interfere with sample analysis shall be corrected prior to sample analysis.

If any of the laboratory's standard QA/QC criteria are stricter than those delineated here, then it is expected that the laboratory will default to their criteria for these sample analyses.

Full data packages shall be provided on CD for all sample analyses to allow for reconstruction of analysis: Chain-of-custody forms, calibration documentation, QA/QC results, raw data, data reduction, data qualifiers, quantitation and detection limits, deviations from method requirements, deviations from QC acceptance criteria, and these deviations' impact to reported results.

Isotech Laboratories will submit a final report at completion of analysis which includes: (1) statements outlining analytical procedures, (2) pretreatments applied, and (3) calendar calibration information.

Sample bags will be purged with laboratory-grade  $\text{N}_2$  at least three times prior to sample collection. Sample container blanks (at least one per every 10 samples) will be collected for both field screening (if sample bags are used) and fixed-laboratory analysis (see **Table 7**) to ensure the absence of cross-contamination.

Detection limits from Isotech Laboratories will be acquired to determine if they meet project objectives.

\* Sample duplicates will be performed on our samples submitted for this work, i.e., sample duplicate results for samples from other sources (for analytical runs that may include samples from other sources) will not be considered for meeting these QC requirements.

### 6.3 Quality Metrics (QA/QC Checks) for Aqueous Analysis

QA/QC requirements (e.g., blanks, calibration checks, duplicates, second source standards, matrix spikes) are described in various in-house Standard Operating Procedures and summarized in **Table 3**. Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results.

Samples will be submitted to Isotech Laboratories for analysis of stable isotope ratios ( $\delta^{13}\text{C}$ ) of dissolved inorganic carbon. A general discussion of their QA/QC is provided in their QAP attached in **Appendix A**. However, acceptance criteria are not included. An inquiry will be made of Isotech for this information.

#### 6.3.a Measured and Calculated Solute Concentration Data Evaluation

The computer program AqQA (RockWare Inc., version 1.1.1) will be used as a check on the quality of solute concentration data. Two methods will be used. First, the specific conductance values measured in the field will be compared to a calculated value that is based on anion- and cation-specific resistivity constants and the measured concentrations of anions and cations in specific ground-water samples. The agreement between the measured and calculated values should be within 15%. The second method will be to calculate the charge balance for each solution. This is done by summing and comparing the net positive and negative charge from the measured concentrations of anions and cations. The agreement should be within 10%. Poor agreement would suggest that some major solute(s) is not accounted for in the analytical measurements. At the discretion of the PI, discrepancies in this manner will be either flagged or the identity of other sample components and/or reason(s) for poor agreement will be investigated.

#### 6.3.b Detection Limits

Detection limits for the various analytes are listed in the Standard Operating Procedures for these methods and are not repeated here. They are adequate for project objectives.

#### 6.3.c QA/QC Calculations

% Recovery or Accuracy

$$\% \text{REC} = (m/n) \times 100$$

Where  $m$  = measurement result

$n$  = True Value (a certified or known value) of standard or reference

Precision

Precision is described by Relative Percent Difference (RPD) as previously defined. The Relative Percent Difference (RPD) is calculated based on the following:

$$RPD = \frac{2|a - b|}{a + b} 100$$

where  $a$  = sample measurement and  $b$  = duplicate sample measurement and  $a > b$ .

## Matrix Spike Recovery

Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results.

$$\% \text{ Recovery} = \frac{\text{spiked sample conc} - \text{native sample conc}}{\text{spiked sample conc}} 100$$

## 7. Data Analysis, Interpretation, and Management

Data validation will consist of initial and final review of data. Initial review will include continuous oversight during field collection of data by the principal investigator to avoid common transcription errors associated with recording of data. Final review will include evaluation of all collected data for suitability in data interpretation. It will include but is not limited to the following activities: (1) assessment of data completeness, (2) review of log books and forms used for data logging, and (3) review of calibration and standard checks.

### 7.1 Data Recording

#### 7.1.a Soil Gas

To ensure collection of all relevant data during each purging event, a spreadsheet, illustrated in **Figure 8**, will be used to manually record readings from the GEM2000 CES LandTec Gas Analyzer. The data will be collected by a technician during testing and reviewed in the field by the principal investigator during and at the cessation of each test. The principal investigator will then convert purging data to an EXCEL spreadsheet for electronic storage and data manipulation. For gas permeability testing, pressure readings will be recorded every second and stored in a file in a PC using a RS232 cable.

#### 7.1.b Water

Data collected during the ground-water investigation will be recorded into field notebooks and entered into EXCEL spreadsheets. Water quality data will also be entered into AqQA a program for evaluating ground water quality and for evaluating data validity. Graphs will be produced using EXCEL or Origin to show key data trends.

### 7.2 Data Storage

As this is a Category I project, all data and records associated with this project will be kept permanently and will not be destroyed. All data generated in this investigation will be stored electronically in Microsoft EXCEL and backed up in RSKERC's local area network 'M' drive. All paper-based records will be kept in the PI's offices. If the project records are archived, Dr. DiGiulio will coordinate with Dr. Wilkin the compiling of all data and records.

### 7.3 Analysis of Data

All data collected associated with ground-water and soil-gas sampling will be summarized in EXCEL spreadsheets. Data in spreadsheets will be spot-checked against original data reports by selecting random data points for comparison to verify accuracy of data transfer. When

possible, data sets will be graphically displayed using EXCEL, Sigma Plot, and Origin to reveal important trends.

## **8.0 Assessment and Oversight**

### **8.1 Assessments**

Technical Systems Audits (TSAs) and Audits of Data Quality (ADQs) will be conducted early in the project to allow for identification and correction of any issues that may affect data quality. TSAs will be conducted on both field and laboratory activities. Detailed checklists, based on the procedures and requirements specified in this QAPP and related SOPs, will be prepared and used during these TSAs. Two field TSAs will be done; one on the soil gas sampling and the other on the ground water sampling. It is anticipated these will take place in late July to September, 2010. The GWERD QA Manager (QAM), Steve Vandegrift, will take the lead on these audits with contract support from Neptune and Co.

Laboratory TSAs will focus on the critical target analytes and will be conducted on-site at GWERD (involves both EPA and contractor-operator labs) and at an off-site contract laboratory which will do the gas and isotope analysis. It is anticipated these will take place in June-August, 2010. At this time, Isotech Laboratories, Inc., in Champaign, IL, is anticipated to be the off-site contract lab. The GWERD QA Manager will take the lead on the TSA with contract support from Neptune and Co. for the off-site contract lab. The on-site lab TSA will be conducted by the GWERD QAM, with assistance from the NRMRL Director of QA, Lauren Drees in the preparation of checklists.

ADQs will be conducted on a representative sample of data for the critical target analytes. These will be performed by the GWERD QAM with assistance from the NRMRL Director of QA. These will begin with the first data sets (July-August, 2010) to ensure there are no issues with the data and to allow for appropriate corrective actions on subsequent data sets if needed.

### **8.2 Assessment Results**

Assessment results will be documented in reports to the PIs and the GWERD Division Director. If any serious problems are identified that require immediate action, the QAM will verbally convey these problems at the time of the audit to the PI.

The PIs are responsible for responding to the reports as well as implementing corrective actions, if needed, in a timely manner to ensure that quality impacts to project results are minimal.

### **8.3 Informing Management**

Meetings will be held at least once per month between NRMRL-Ada staff and EPA Region VIII management to keep Region VIII management informed of technical activities.

## **9.0 Reporting**

The principal investigator and co-principal investigator will summarize and interpret data collected for EPA Region VIII to allow incorporation into a comprehensive report being developed by EPA Region VIII. The final product(s) for NRMRL-Ada could be one or more journal articles describing



activities and findings at the site. However, these publications would have to be cleared through EPA Region VIII.

## 10.0 References

- Azzaro, R., S. Branca, S. Giammanco, S. Gurrieri, R. Rasa, and M. Valenza. 1998. New evidence for the form and extent of the Pernicana Fault System (Mt. Etna) from structural and soil-gas surveying. *Journal of Volcanology and Geochemical Research*, 84:143-152.
- Baldassare, F.J., and C.D. Laughrey. 1997. Identifying the sources of stray methane by using geochemical and isotopic fingerprinting. *Environmental Geosciences*, v. 4, no. 2, p. 85-94.
- Baubron, J.C., A. Rigo, and J.P. Toutain. 2002. Soil gas profiles as a tool to characterize active tectonic areas: the Jaut Pass example (Pyrenees, France). *Earth and Planetary Science Letters*, 196:69-81.
- Ciotoli, G., S. Lombardi, A. Annunziatellis. 2007. Geostatistical analysis of soil gas data in a high seismic intermontane basin: the Fucino Plain, central Italy. *Journal of Geophysical Research*, 112(B05407), doi:10.1029/2005JB004044.
- Ciotoli, G., S. Lombardi, S. Morandi, and F. Zarlunga. 2004. A multidisciplinary statistical approach to study the relationships between helium leakage and neotectonic activity in a gas province: The Vasto basin, Abruzzo-Molise (central Italy). *The American Association of Petroleum Geologists Bulletin*, 88(3):355-372.
- Ciotoli, G., M. Guerra, S. Lombardi, and E. Vittori. 1998. Soil gas survey for tracing seismogenic faults: A case study the Fucino basin (central Italy). *Journal of Geophysical Research*, 103(B10):23, 781-783, 794.
- Ciotoli, G., G. Etiope, M. Guerra, and S. Lombardi. 1999. The detection of concealed faults in the Ofanto basin using the correlation between soil-gas fracture surveys. *Tectonophysics*, 299(3-4):321-332.
- DiGiulio, D.C. and R. Varadhan. 2001. Development of recommendations and methods to support assessment of soil venting performance and closure. EPA/600/R-01/070. (<http://www.epa.gov/ada/pubs/reports.html>)
- Fountain, J.C. and R.D. Jacobi. 2000. Detection of buried faults and fractures using soil gas analysis. *Environmental and Engineering Geoscience*, 6(3):201-208.
- Fridman, A.I., 1990. Application of naturally occurring gases as geochemical pathfinders in prospecting for endogenetic deposits. *Journal of Geochemical Exploration*, 38(1-2):1-11.
- Janezic, G.G. 1979. Biogenic light hydrocarbon production related to near-surface geochemical prospecting for petroleum. *The American Association of Petroleum Geologists Bulletin*, 63:403.
- Jones, V.T. and R.J. Dozd. 1983. Predictions of oil and gas potential by near-surface geochemistry. *The American Association of Petroleum Geologists Bulletin*, 67(6):932-952.
- Jones, V.T., and R.J. Pirkle. 1981. Helium and hydrogen soil gas anomalies associated with

deep or active faults. Presented to the American Chemical Society, March 29 - April 3, 1981, Atlanta, Georgia

Jones, V.T. and Pirkle. 2009. Application of Exploration Geochemical Methodology to CO<sub>2</sub> Monitoring, Lawrence Berkeley National Laboratory, BNL Subcontract No. 6804108.

Kaplan, I.R., Y. Galperin, S. Lu, and R. Lee. 1997. forensic environmental geochemistry- Differential of fuel-types, their sources, and release time, *Oragnaic Geochemistry*, v. 27, no. 5/6, p.289-317.

King, C.Y., B.S. King, W.C. Evans, and W. Zang. 1996. Spatial radon anomalies on active faults in California. *Applied Geochemistry*, 11:497-510.

LeNeveu, D.M. 2008. CQUESTRA, A risk and performance assessment code for geological sequestration of carbon dioxide. *Energy Conversation & Management*, 49:32-46.

Lewicki, J.L. and S.L. Brantley. 2000. CO<sub>2</sub> degassing along the San Andreas fault, Parkfield, California. *Geophysical Research Letters*, 27(1):5-8.

Lewicki, J.L., W.C. Evans, G.E. Hilley, M.L. Sorey, J. Rogie, and S.L. Brantley. 2003. Shallow soil CO<sub>2</sub> flow along the San Andreas and Calaveras Faults, California. *Journal of Geophysical Research*, 108(B4):2187, doi:10.1029/2002JB002141.

New York State Department of Health, Center for Environmental Health, Bureau of Environmental Exposure Investigation. Guidance for Evaluating Soil Vapor Intrusion in the State of New York, October, 2006.

Nordbotten, J.M., M.A. Celia, and S. Bachu. 2004. Analytical solutions for leakage rates through abandoned wells. *Water Resources Research*, 40, W04204, doi:10.1029/2003WR002997.

Nordbotten, J.M., M.A. Celia, and S. Bachu. 2005a. Injection and storage of CO<sub>2</sub> in deep saline aquifers: Analytical solution for CO<sub>2</sub> plume evolution during injection. *Transport Porous Media*, 58:339-360.

Nordbotten, J.M., M.A. Celia, S. Bachu, and H.K. Dahle. 2005b. Semianalytical solution for CO<sub>2</sub> leakage through an abandoned well. *Environmental Science & Technology*, 39:602-611.

Rowe, D. and K. Muehlenbachs. 1999. Isotopic fingerprinting of shallow gases in the Western Canadian sedimentary basin-Tools for remediation of leaking heavy oil wells. *Organic Geochemistry*, v. 30, p. 861-871.

Schoell, M. 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origin. *Geochimica et Cosmochimica Acta*, v. 44, p. 649-661.

Schoell, M. 1983. Genetic characteristics of natural gases. *American Association of Petroleum Geologists Bulletin*, v. 67, no. 12, p. 2225-2238.

Thien, S.J. 1979. A flow diagram for teaching texture by feel analysis. *Journal of Agronomic Education*. 8:54-55.

Wakita, H., et al., 1980. Hydrogen release: New indicator of fault activity. *Science*, 210:188-190.

Wakita, H., et al., 1978. Helium spots: Caused by diapiric magma from the upper mantle. *Science*, 200:430-432.

### **Standard Operating Procedures**

RSKSOP-102v5 - *Determination* of Total Carbon, Total Organic Carbon, Dissolved Carbon, and Dissolved Organic Carbon in Water using the Dohrmann DC-80 Carbon Analyzer 17 p.

RSKSOP-175v4 - Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, 16p.

RSKSOP-194v4 - Gas Analysis by Micro Gas Chromatographs (Agilent Micro 3000), 13p.

RSKSOP-213v4 - Standard operating procedure for operation of Perkin Elmer Optima 3300 DV ICP-OES, 21 p.

RSKSOP-214v5, Quality control procedures for general parameters analysis using Lacjhat Flow Injection analysis (FIA), 10p.

RSKSOP-257v2, Standard operating procedure for elemental analysis by ICP-MS, 16 p.

RSKSOP-276v3 - Determination of major anions in aqueous samples using capillary ion electrophoresis with indirect UV detection and Empower 2 software, 11 p.

RSKSOP-296v0 - Determination of hydrogen and oxygen isotope ratios in water samples using high temperature conversion elemental analyzer (TC/EA), a continuous flow unit, and an isotope ratio mass spectrometer (IRMS), 8p.

RSKSOP-298v1 - Arsenic Speciation Determination by LC/ICP-MS with Anion Suppression and NaOH Mobile Phase, 21 p.

RSKSOP-313v1 - Determination of R-123 using the H25-IR Infrared Refrigerant Gas Leak Detector, 12p.

RSKSOP-314v1 - Determination of Fixed Gases using the GEM2000 and GEM2000 Plus Gas Analyzers & Extraction Monitors, 13p.

RSKSOP-315v1 – Determination of Carbon Monoxide Using the Bacharach PCA2 Portable Combustion Analyzer, 13p.

RSKSOP-320v0 - Determination of Organic and Inorganic Vapors Using the TVA-1000B Toxic Vapor Analyzer, 18p.

**Table 1.** Tentative schedule of field activities at Pavillion, WY

<b>Activity</b>	<b>04/10</b>	<b>05/10</b>	<b>06/10</b>	<b>07/10</b>	<b>08/10</b>	<b>9/10</b>
Site Reconnaissance	X					
Monitoring Well installation			X	X		
Ground-Water Sampling				X	X	
Cali-5 Bond Sample Bag Study			X			
Soil-Gas Survey/ Installation of Probes				X		
Soil-Gas Sampling (probes)						X

**Table 2.** Ground Water Sample Collection

Measurement	Analysis Method	Sample Container	Preservation/ Storage	Holding Time(s)
Dissolved gases	RSKSOP-194v4 &-175v4*/**	150 mL stainless steel (SS) sampling vessel for deep wells & 60 mL serum bottles for tap water samples	Spare tap water samples preserved with/TSP† to compare w/unpreserved; Refrigerate at 4°C	<14 days**
Metals	RSKSOP-213v4 &-257v2	125 mL Plastic bottle	HNO <sub>3</sub> pH<2	6 months (Hg 28 days)
As speciation	RSKSOP-298v1	30 mL amber plastic	HCl pH<2; refrigerate at 4°C	8 days
SO <sub>4</sub> , Cl, F	RSKSOP-276v3	30 mL clear plastic	Refrigerate at 4°C	28 days
NO <sub>3</sub> + NO <sub>2</sub> , NH <sub>4</sub>	RSKSOP-214v5	30 mL clear plastic	H <sub>2</sub> SO <sub>4</sub> pH<2; refrigerate at 4°C	28 days
Dissolved DIC/DOC	RSKSOP-102v5	45 mL glass VOA vial	No headspace; refrigerate at 4°C	28 days
δ <sup>13</sup> C of dissolved inorganic carbon	Isotech: gas stripping & IRMS	100 mL glass bottle	Refrigerate at 4°C	No information
O, H stable isotopes of water	RSKSOP-296v0	20 mL glass VOA vial	Refrigerate at 4°C	Stable
Organics (Region 8)	NA	1L bottles to be provided by R8 or R8 provided requirement for bottles	Refrigerate at 4°C	NA

\*RSKSOP-175v4 appropriate for samples in serum bottles, not the SS sample vessels

\*\*14 days w/acid or trisodium phosphate preservation; holding time not established w/o preservation; comparison will be made between preserved and unpreserved tap water samples.

† trisodium phosphate

**Table 3.** Groundwater Laboratory QA/QC Requirements Summary\* from SOPs

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Dissolved gases	RSKSOP-194v4 & 175v4*	≤MDL  (He blank, first and last in sample queue; water blank before samples)	85-115% of known value  (After helium blank at first of analysis queue, before helium blank at end of sample set, and every 15 samples)	85-115% of known value  (After first calibration check)	RPD≤20  (Every 15 samples)	NA
Metals	RSKSOP-213v4	<QL for 80% of metals (Beginning and end of each sample queue)	90-110% of known value ( Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after calibration check)	RPD<20 for 80% of metals  (Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (at least one per matrix type)
Metals	RSKSOP-257v2	<QL for 80% of metals; none >10x MDL (Beginning and end of each sample queue)	90-110% of known value ( Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after first calibration check)	RPD<20 for 80% of metals  (Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 70-130% Rec. (at least one per matrix type)
As speciation	RSKSOP-298v1	<½QL (after initial calib., every 10-15 samples, and at end)	80-120% of known value (after initial calib., every 10-15 samples, and at end)	80-120% of known value (Immediately after calibration)	RPD<20  (Every 15 samples)	80-120% Rec. (one per 20 or every set)
SO <sub>4</sub> , Cl, F	RSKSOP-276v3	<MDL (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 15 samples)	80-120% Rec. (one per every 20 samples)

NO <sub>3</sub> + NO <sub>2</sub> , NH <sub>4</sub>	RSKSOP- 214v5	<½ lowest calib. std. (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 10 samples)	80-120% Rec. (one per every 20 samples)
Dissolved DIC/DOC	RSKSOP- 102v5	<½QL (after initial calib., every 10-15 samples, and at end)	80-120% of known value (after initial calib., every 10-15 samples, and at end)	80-120% of known value (Immediately after calibration)	RPD<10 (every 15 samples)	80-120% Rec. (one per 20 or every set)
O, H stable isotopes of water	RSKSOP- 296v0	NA	Difference of calibrated/true < 3‰ for δ <sup>2</sup> H & < 1‰ for δ <sup>18</sup> O	Working stds calibrated against IAEA stds.	Standard deviation ≤ 3‰ for δ <sup>2</sup> H and < 1‰ for δ <sup>18</sup> O (every sample)	NA
δ <sup>13</sup> C of dissolved inorganic carbon	Isotech: gas stripping & IRMS	NA	Referenced to δ <sup>13</sup> C of the Peedee belemnite (NIST material); Difference of calibrated/true < 1‰ for δ <sup>13</sup> C	80-120% of known value (Immediately after calibration)	RPD<10 (every 15 samples)	NA

\*This table only provides a summary; SOPs should be consulted for greater detail.

Corrective actions are outlined in the SOPs.

MDL = Method Detection Limit

QL = Quantitation Limit

PE = Performance Evaluation

\*\*RSKSOP-174v4 will need to be modified to accommodate samples collected from deep wells in the sample bombs

**Table 4.** Summary of analytes, instruments, use, calibration, and check standards for portable gas analyzers

Analyte	Instrument (Detector)	Method	Range	Calibration	Check Standard	Accuracy
O <sub>2</sub>	GEM-2000 Plus CES-LANDTEC (EC Cell)	RSKSOP-314v1	0 - 21%	4%, 10%	10%, 20.9%	±1.0% (0-5%) ±1.0% (5-21%)
CH <sub>4</sub>	GEM-2000 Plus CES-LANDTEC (IRGA)	RSKSOP-314v1	0 - 100%	2.5%, 50%	2.5%, 50%	±0.3% (0-5%) ±1% (5-15%) ±3% (15-100%)
CO <sub>2</sub>	GEM-2000 Plus CES-LANDTEC (IRGA)	RSKSOP-314v1	0 - 100%	5%, 20%, 35%	5%, 20%, 35%	±0.3% (0-5%) ±1.0% (5-15%) ±3.0% (15-50%)
CO (tracer)	Bacharach PCA2 Portable Combustion Analyzer (IRGA)	RSKSOP-315v1	0 – 20,000 ppmv	4,000 ppmv	4,000, 18,000 ppmv	±5% or ± 10 ppmv whichever is greater (0-2000 ppmv) ±10% (2,000-10,000 ppmv)
CO (tracer)	GEM-2000 Plus CES-LANDTEC (EC Cell)	RSKSOP-314v1	0 – 2000 ppmv	100 ppmv	100, 500, 1000 ppmv	±10% (0-2000 ppmv)
R-123 (tracer)	Bacharach H25-IR Industrial Refrigerant Leak Detector (IRGA)	RSKSOP-313v1	0 – 10,000 ppmv	Internal source (25.3 ppmv)	200, 1000 ppmv	±10% (0-1000 ppmv)
H <sub>2</sub> S	GEM-2000 Plus CES-LANDTEC (EC Cell)	RSKSOP-314v1	0 – 500 ppmv	100 ppmv	25,100, and 200 ppmv	±10% (0-500 ppmv)
H <sub>2</sub>	GEM-2000 Plus CES-LANDTEC (EC Cell)	RSKSOP-314v1	0 – 1000 ppmv	100 ppmv	100, 500 ppmv	±10% (0-1000 ppmv)
VOCs	Thermo Scientific TVA-1000B (FID)	RSKSOP-320v0	1.0 – 10,000 ppmv	0.0, 10, 100, 1000, 9000 ppmv CH <sub>4</sub>	10, 100, 1000, 9000 ppmv CH <sub>4</sub>	±25% or ±2.5 ppmv, whichever is greater, from 1.0 to 10,000 ppmv.
VOCs	Thermo Scientific TVA-1000B (PID)	RSKSOP-320v0	0.5 – 500 ppmv	0.0, 250, 475 ppmv	250, 475 ppmv Isobutylene	±25% or ±2.5 ppmv, whichever is greater, from 0.5 to 500 ppmv.



**Table 5. Soil Gas Sample Field Screening Methods and QA/QC Requirements\* from SOPs**

Measurement	Analysis Method	Blanks** (Frequency)	Calibration Check Standards (Frequency)	Second Source Standards (Frequency)
O <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub> ,	RSKSOP-314v1	0 (beginning & end of each sample event)	+/-1% of reading  (beginning & end of each sample event)	+/-1% of reading  (after each calibration, optional for this project)
CO, H <sub>2</sub> S, (H <sub>2</sub> ***)	RSKSOP-314v1	0 (beginning & end of each sample event)	+/-1% of reading  (beginning & end of each sample event)	NA
CO	RSKSOP-315v1	0 (beginning & end of each sample event)	90-110% of known value  (after calibration, beginning & end of each sample event)	NA
R-123	RSKSOP-313v1	0 (beginning & end of each sample event)	90-110% of known value  (after calibration, beginning & end of each sample event; every 2 hours)	NA
Total Hydrocarbons	RSKSOP-320v0	0 (beginning & end of each sample event)	90-110% of known value  (after calibration, beginning & end of each sample event)	NA

Corrective actions are detailed in the SOPs.

\*Duplicate sample not appropriate for measurements from a sample train.

\*\*Meter readings

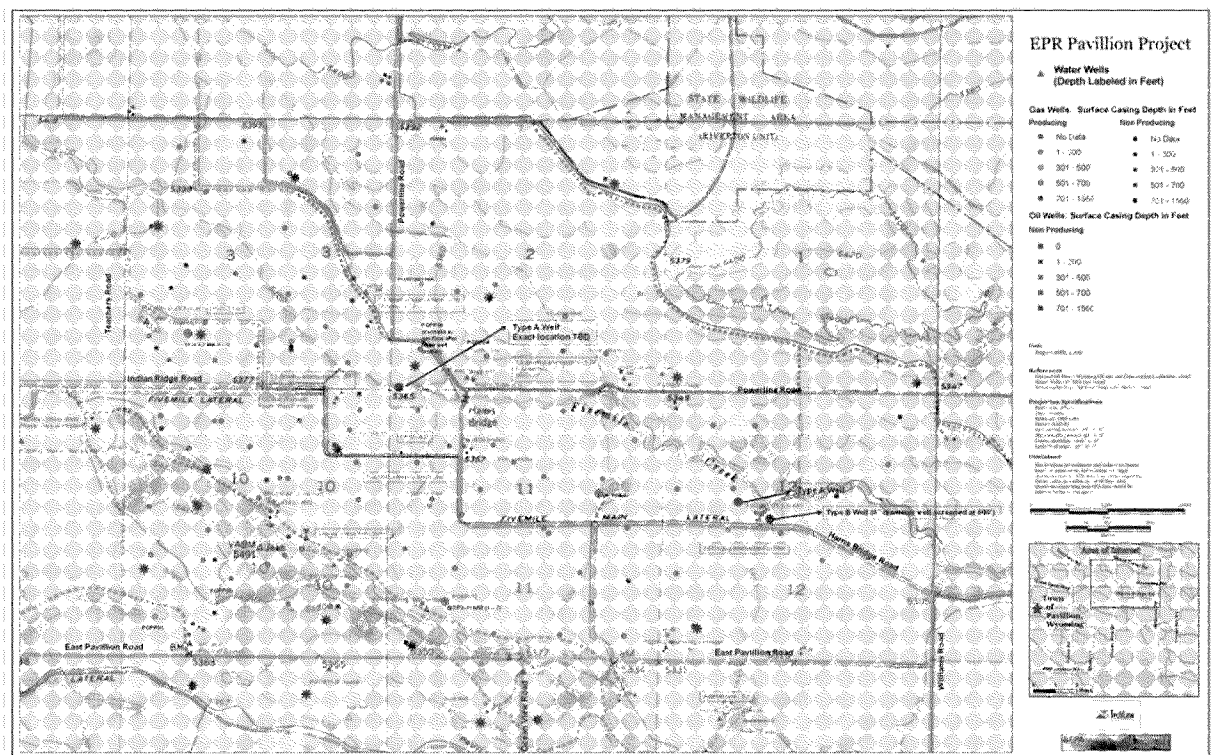
\*\*\*to be added to SOP later

**Table 6. Soil Gas Sample Fixed Laboratory Methods and QA/QC Requirements**

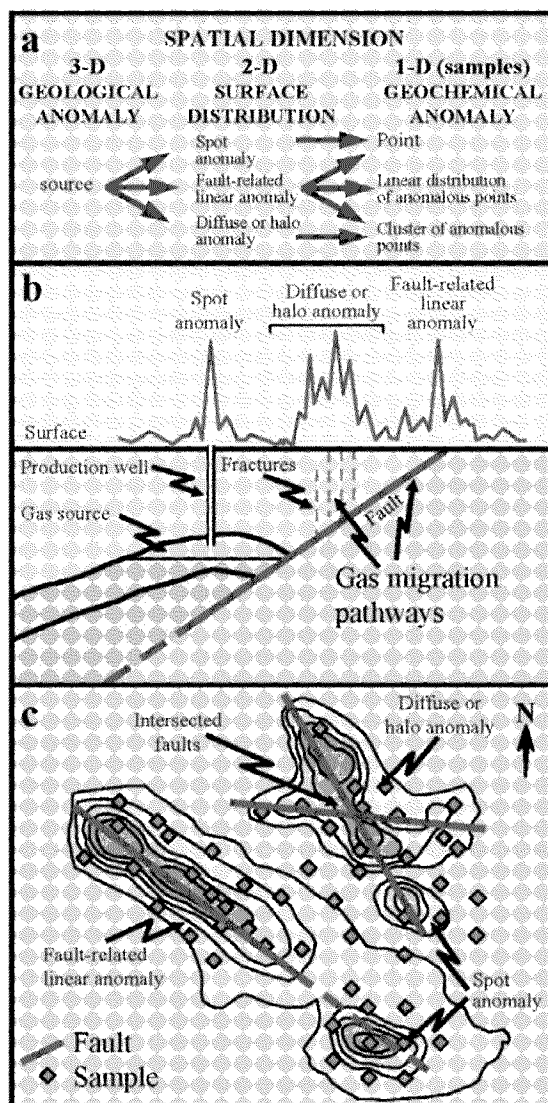
Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Ar, He, H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>3</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , iC <sub>4</sub> H <sub>10</sub> , nC <sub>4</sub> H <sub>10</sub> , iC <sub>5</sub> H <sub>12</sub> , nC <sub>5</sub> H <sub>12</sub> , C <sub>6</sub> <sup>+</sup>	Modification of ASTM D1945-03	None Detected  (after calibration, every 10 samples, end of run)	85-115%  (after calibration, every 10 samples, end of run)	85-115%  (after each calibration)	RPD <15%  (every 10 samples)	NA
Δ <sup>13</sup> C and δD of CH <sub>4</sub> and δ <sup>13</sup> C for CO <sub>2</sub>	Gas stripping and IRMS	Will obtain from Isotech  (after calibration)	≤0.5 per mil  (after calibration, every 10 samples, end of run)	≤0.5 per mil  Will obtain from Isotech	≤0.5 per mil  (every 5 samples)	NA
Δ <sup>14</sup> C for CH <sub>4</sub>	Will obtain from Isotech	< 0.35 pMC  Will obtain from Isotech	+/- 1 pMC  Will obtain from Isotech	+/- 1 pMC  Will obtain from Isotech	Will obtain from Isotech NA	

**Table 7.** Summary of quality control samples, purpose, method, and frequency to support gas analysis at a fixed laboratory.

<b>QC Sample</b>	<b>Purpose</b>	<b>Method</b>	<b>Frequency</b>	<b>Acceptance Criteria</b>
Equipment Blanks	Ensure that construction materials in gas sample bags and the sample train are not a source of vapors or gases of concern	Fill sample bags with zero-grade N <sub>2</sub> gas via the sample train.	One sample per day	< Detection limit
Travel Blanks	Ensure that cross-contamination does not occur during sampling or transport to the laboratory	Fill sample bags with zero-grade N <sub>2</sub> gas and place in shipping container with other samples.	One sample per shipment	< Detection limit
Duplicates	Check precision of sampling method and analysis	Use a tee to collect two samples simultaneously.	One sample every 10 samples	RPD < 20%

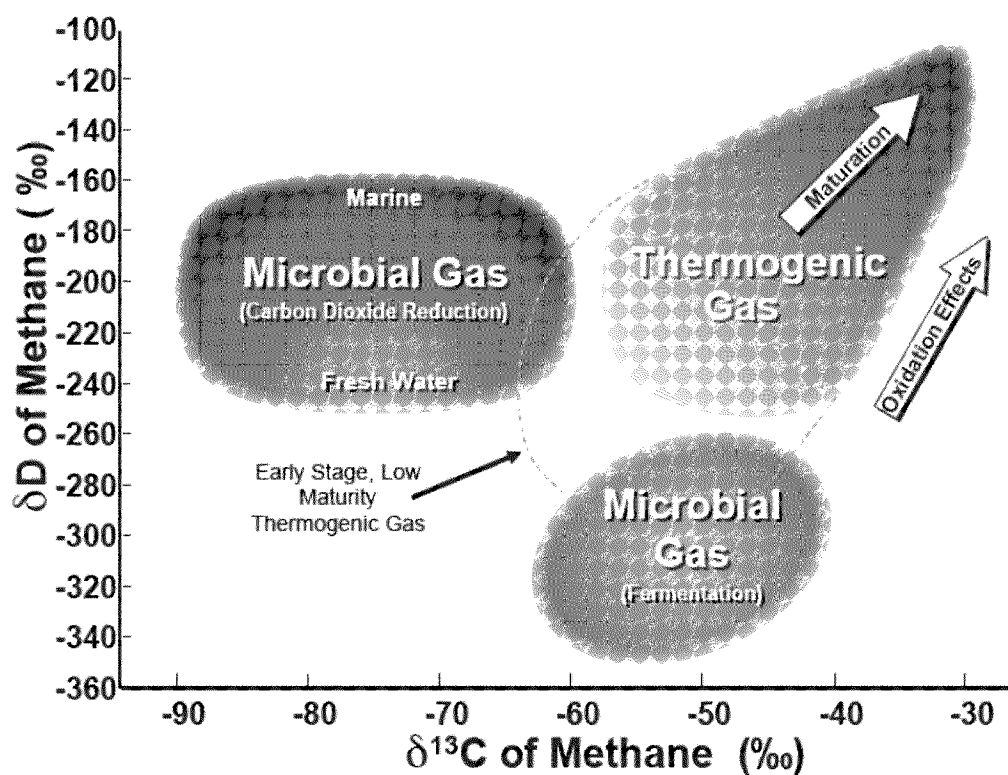


**Figure 1.** Outline of study area and location of Type A and B monitoring wells



**Figure 2.** Different types of geochemical anomalies in relation to their spatial dimension (a). Frames (b) and (c) show section and plan view, respectively, of the possible types of geochemical anomalies occurring in faulted areas. Frame (b) shows the case of a gas reservoir confined in a structural trap by low-angle faults, which constitute enhanced permeability pathways for gas migration toward the surface. At the surface, this causes anomalies with different geometry (being the surface expression of fractures and faults), as well as their shifting some distance away from the gas source. In some cases, the anomaly could be the direct result of production activity (i.e., spot anomaly) (From Ciotoli et al., 2004).

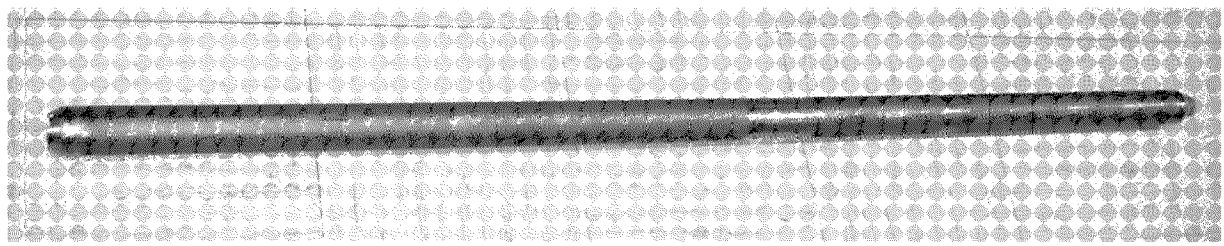
## Fingerprinting of Gases



**Figure 3.** Plot of  $\delta^{13}\text{C}$  versus  $\delta\text{D}$  for methane to discern the origin of methane. Figure from Isotech Laboratories.

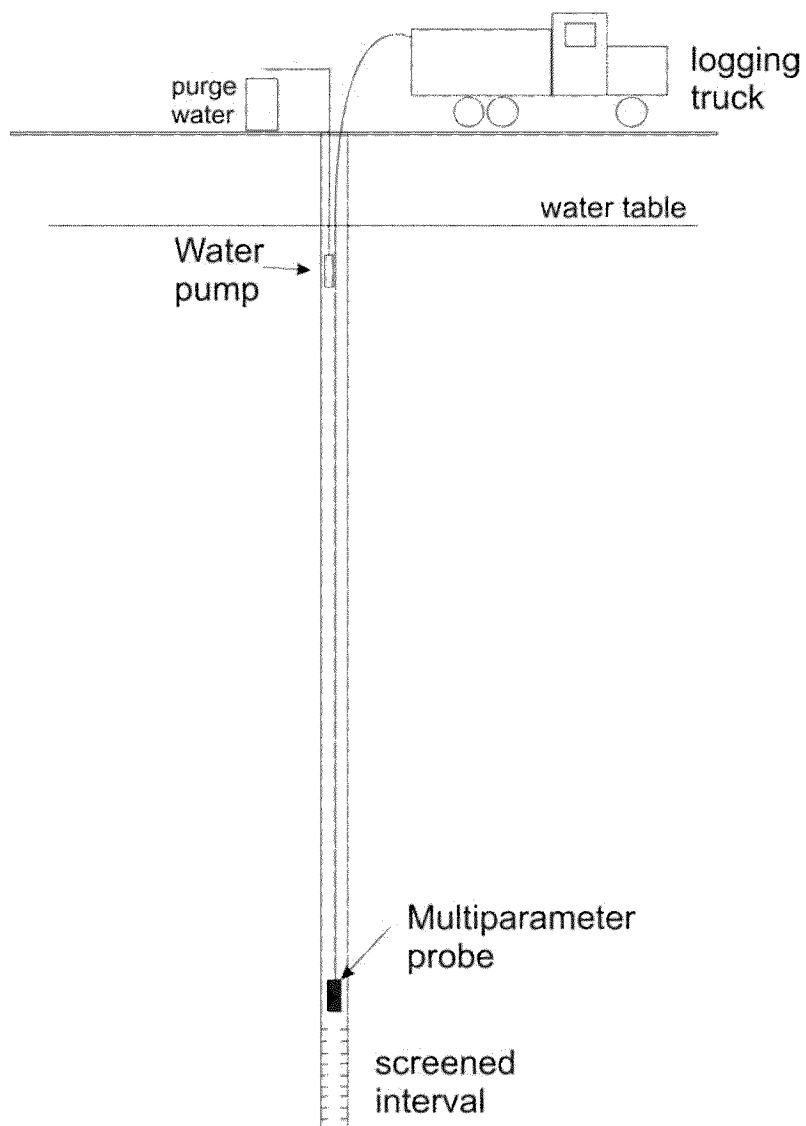
ERATHEM	SYSTEM	GEOLOGIC UNIT	HYDROLOGIC ROLE
CENOZOIC	Quaternary	Deposits including: alluvial, colluvial, terrace, pediment, landslide, glacial, and travertine	Local aquifers
	Tertiary	Wiggins Formation	Leaky confining layer
		Tepee Trail Formation	
		Aycross Formation	
		Wind River Formation	Aquifer
MESOZOIC	Upper Cretaceous	Indian Meadows Formation	Leaky confining layer
		Fort Union Formation	Aquifer
		Lance Formation	
		Meeteetse Formation	Leaky confining layer
		Mesaverde Formation	Aquifer
		Cody Shale	
		Niobrara Formation	Leaky confining layer
		Frontier Formation	Aquifer
	Lower Cretaceous	Mowry Shale	Leaky confining layer
		Muddy Sandstone	Aquifer
		Thermopolis Shale	Leaky confining layer
		Cloverly Formation	Aquifer
	Jurassic	Morrison Formation	Leaky confining layer
		Sundance Formation	Aquifer
		Gypsum Spring Formation	Leaky confining layer
		Nugget Sandstone	Aquifer
	Triassic	Chugwater Group	Leaky confining layer
		Popo Agie Formation	
		Crow Mountain Formation	
		Alcova Limestone	
PALEOZOIC	Permian	Dinwoody Formation	Aquifer
		Phosphoria Formation	Leaky confining layer
	Pennsylvanian	Park City Formation	Aquifer system
		Tensleep Sandstone	
	Mississippian	Darwin Sandstone Member	
		Amsden Formation	
	Devonian	Madison Limestone	
	Silurian	Darby Formation	
	Cambrian	Bighorn Dolomite	Leaky confining layer
		Gallatin Limestone	
		Gros Ventre Formation	
		Flathead Sandstone	Aquifer
	Precambrian		

**Figure 4.** Stratigraphic section and hydrologic roles of rocks on the Wind River Indian Reservation, Wyoming. From USGS (2005)



**Figure 5.** Photograph of bomb sampler to be used to sample water from Type A and Type B monitoring wells





**Figure 6.** Sample train for ground-water sampling

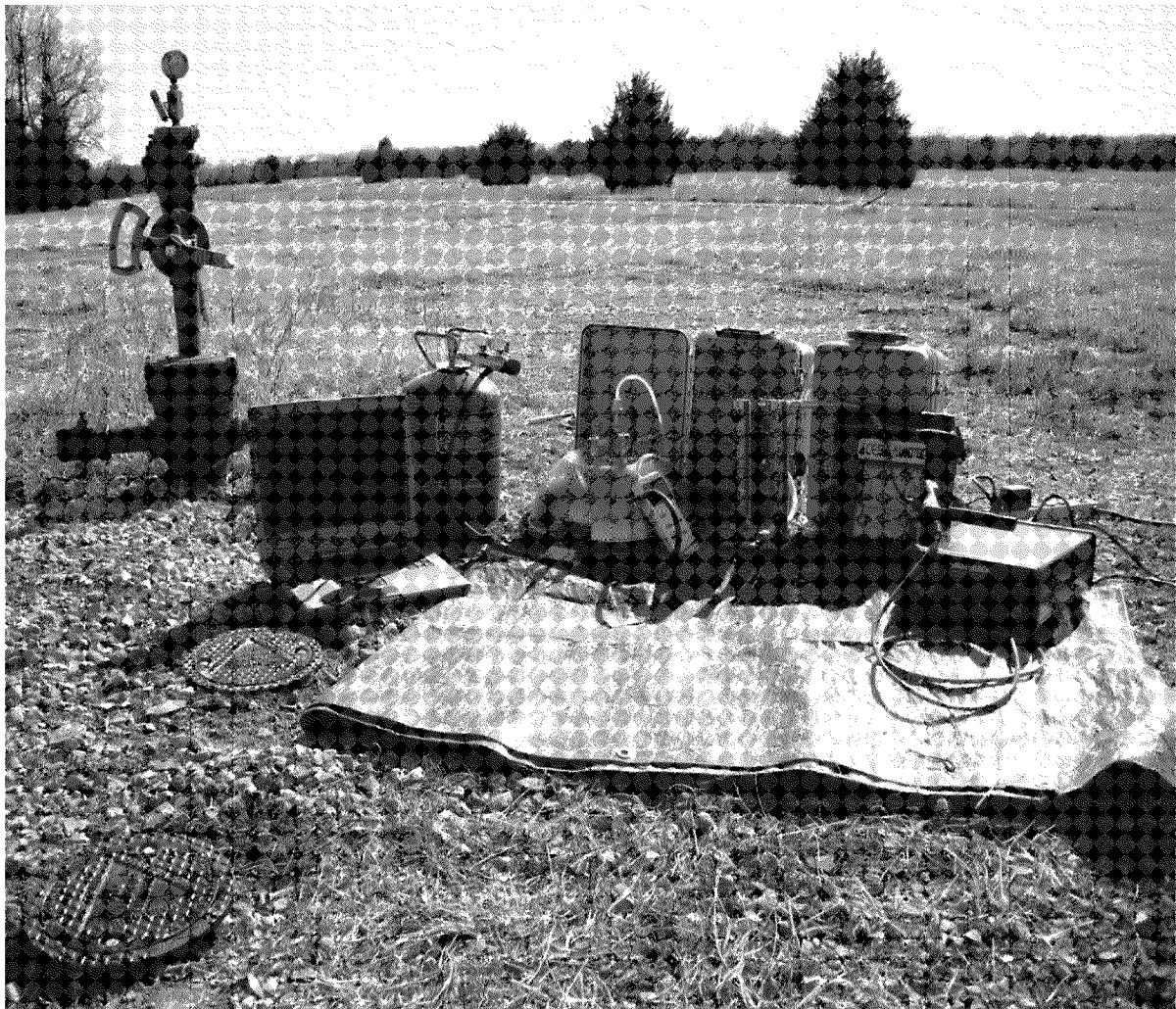


## Sample Analysis Request and

## Chain of Custody (COC) Record

[illegible]

**Figure 7.** Chain of Custody form for submittal of water samples to R.S. Kerr Environmental Research Center.



**Figure 8.** Phototgraph of soil-gas sampling train

**Figure 9.** Spreadsheet for manually recording readings from the LANDTEC-CES GEM2000 Plus Gas Analyzer



**Send Data and Invoice to**

Name: \_\_\_\_\_  
 Company: \_\_\_\_\_  
 Address: \_\_\_\_\_  
 \_\_\_\_\_  
 Phone: \_\_\_\_\_  
 Fax: \_\_\_\_\_  
 Email: \_\_\_\_\_

Project: \_\_\_\_\_  
 Purchase Order #: \_\_\_\_\_  
 Location: \_\_\_\_\_  
 Sampled By: \_\_\_\_\_  
Circle one    Standard  
                     Priority  
                     Rush

**Sample Description**

				Analyte Requested			Comments
Container Number	Sample Identification	Date Sampled	Time				

**Chain-of-Custody Record**

Signature	Company	Date	Time
Relinquished by			
Received by			
Relinquished by			
Received by			
Relinquished by			
Received by			

**Figure 10.** Chain of Custody form for submittal of soil-gas samples to Isotech Laboratories

## Material Safety Data Sheet (MSDS)

### SECTION I

**TRADE NAME:** Gas Samples, non-pressurized, flammable (UN3167)

**CHEMICAL NAME AND SYNONYMS:** Methane Gas, Hydrocarbon Gas Mixture, Natural Gas

### SECTION II -

#### HAZARDOUS INGREDIENTS

Methane (CAS 74-82-8)	5 - 99%
Carbon dioxide (CAS 124-38-9)	0 - 50%
Nitrogen (CAS 124-38-9)	0 - 95%
Ethane (CAS 74-84-0)	0 - 10%
Propane (CAS 74-98-6)	0 - 5%
Butane (CAS 106-97-8)	0 - 2%
C <sub>4</sub> H <sub>10</sub> (CAS 106-97-8)	0 - 1%

Gas samples may also contain trace quantities (<0.1%) of various organic gases not listed above.

### SECTION III - PHYSICAL DATA

**Solubility:** appreciable

**Appearance (Color, Odor, etc.):** colorless, tasteless and normally odorless gas, however may have a characteristically organic odor.

**Boiling Point:** less than -250°F

**Specific Gravity:** see Gas Density

**Vapor Pressure:** not established

**Percent Volatile (Volume %):** 100

**Evaporation:** n/a

**Gas Density:** 0.6 to 1.2 (air = 1.0)

### SECTION IV -

#### FIRE AND EXPLOSION HAZARD DATA

Gas Samples can present a fire hazard. Being a mixture, the gas can explode violently on contact with any source of ignition.

**Flash Point:** less than -305°F (est.)

**Autoignition Temp.:** approx. 930°F

**Flammability Limits:** LEL 5% to UEL 15%

**Extinguishing Media:** Carbon dioxide or dry chemical.

**Special Fire Fighting Procedures:** For fires involving this material, do not enter any enclosed or confined fire space without proper protective equipment. Read the entire MSDS.

### SECTION V

#### HEALTH HAZARD INFORMATION

**Eye Contact:** Not expected to cause eye irritation.

**Skin Contact:** Not expected to be irritating to the skin.

**Inhalation:** Breathing high concentrations of gas samples is not expected.

**Chronic Effects:** Not expected.

#### EMERGENCY FIRST AID PROCEDURES

**Eye Contact:** If irritation occurs, flush eyes immediately with fresh water for at least 15 minutes while holding the eyelids open.

If irritation continues, seek medical attention.

**Skin Contact:** Not applicable

**Inhalation:** Not applicable

**Ingestion:** Not applicable

### SECTION VI - REACTIVITY DATA

**Stability (Thermal, Light, etc.):** Stable, avoid heat, sparks and open flame.

**Incompatibility (Materials to Avoid):** Oxidizers

**Hazardous Decomposition Products:** Combustion may produce carbon monoxide, carbon dioxide, ethylene, and acetylene.

**Hazardous Polymerization:** Will not occur.

**SECTION VII -****SPILL OR LEAK PROCEDURES**

Eliminate all sources of ignition in vicinity of released gas. Stop gas flow if it can be done without risk. Ventilation is required to keep concentrations below the explosive range.

Waste Disposal Methods: Burn through a flare stack in accordance with federal, state and local regulations.

**SECTION VIII -****SPECIAL PROTECTIVE INFORMATION**

Eye Protection: No special eye protection is required.

Skin Protection: No special skin protection is required.

Respiratory Protection: No special respiratory protection is normally required.

**SECTION IX - SPECIAL PRECAUTIONS**

Flammable gas. Ground all lines and equipment used with gas to prevent static sparks. Do not smoke where gas is used or stored. A 19.5% oxygen concentration in air is the minimum recommended for working without special breathing equipment.

n/a = Not Applicable

The information contained herein has been developed based upon current available scientific data. New information may be developed from time to time which may render the conclusions of this report obsolete. Therefore, no warranty is extended as to the applicability of this information to the users intended purpose or for the consequences of its use or misuse.

**Figure 11** MSDS to accompany soil-gas samples exceeding 5% methane.

## **APPENDIX A**

**See accompanying pdf file “Appendix A Isotech QAP”**



# **QUALITY ASSURANCE PLAN**

for

Isotech Laboratories, Inc.  
1308 Parkland Court  
Champaign, IL 61821

Revised May 21, 2009

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President and Laboratory Director

Date

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Laboratory Manager and QA/QC Officer

Date

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## GENERAL QA/QC PROCEDURES

### 1. SAMPLES

**1.1 Sampling Procedures** It is the responsibility of the person collecting a sample to follow a sound sampling procedure. This will ensure that the sample collected is representative of the whole. Unless employees of Isotech do the sample collection, the entire responsibility for sample collection resides with the client. However, we at Isotech in addition to being available for sample collection, will provide advice on sampling methods, sample storage procedures, and sample size requirements.

**1.2 Sample Containers** Sample containers should be matched in size, type and condition to the anticipated analysis that will give best representation of the source, while preserving the sample integrity prior to analysis. Unless sample containers are provided by Isotech, the responsibility for adequate containers resides with the client. Again, in addition to being able to provide appropriate sample containers, shipping cartons and shipping instructions, Isotech will provide advice on sample containers/cartons and shipping procedures.

**1.3 Sample Custody** A completed "Chain of Custody" record is the responsibility of the client and, if required, should be submitted with the samples. Isotech will provide a "Chain of Custody/Request for Analysis" form if needed. Isotech assumes full responsibility for all samples received and stored for analysis at our laboratory. If any samples are removed from Isotech for additional analysis at other laboratories, a "Chain of Custody" form will be completed. All samples received for analysis are assigned a unique, non-duplicated laboratory number which is used as an identifier for each analysis performed.

### 2. INSTRUCTIONS AND PROCEDURES

**2.1 Instrument Operation Procedures** Analyses performed with manufactured analysis instruments are carried out by the methods either specified or recommended by the manufacturer of the instrument as identified in the instrument manual or provided by on-site training through the manufacturer's service technicians. Much of the operation of these instruments is controlled by personal computers utilizing software written and licensed by the manufacturers.

**2.2 Analytical Procedures** The analytical procedures used routinely at Isotech are described in written standard operating procedures (SOP's) for each analysis. Additional procedures may be used, as needed, in the process of satisfying a client's specific analysis requirements. These procedures will either follow published analytical methods, or methods developed at Isotech for a specific analysis. If the Isotech developed procedure becomes routine, then a standard operating procedure is written. All procedures are reviewed and approved by the laboratory supervisors. Various procedural tests and verifications performed are recorded in bound maintenance log books.

### 3. CALIBRATION AND STANDARDIZATION

**3.1 Calibration Procedure and Frequency** Depending on the analytical technique, instruments used for quantitative analyses are either calibrated at the beginning of every operating period or the calibration is checked by using a reference sample or a calibration standard. The instrument calibration is also checked at appropriate intervals during analyses. Specific instruments that form components of a sample preparation system are calibrated using duplicate sample analysis as well as analysis of a reference sample at appropriate intervals. Records of calibration results are kept in laboratory notebooks or other secure medium (see Documentation).

**3.2 Method Validation** Analytical methods are validated by one or more of the following techniques:

3.2.1 check or reference samples are analyzed and the results are compared with the internal documented or external certified (primary and secondary standards) values,

3.2.2 results from the candidate method are compared with those from another method known to be applicable and reliable, or

3.2.2 spiked samples and surrogate samples are analyzed and the method results are compared with the known concentrations.

**3.3 Check/Reference Samples** A check/reference sample is re-analyzed approximately every tenth analysis. This, in essence, results in a test of the method. Check/reference samples are chosen which have been analyzed many times over a period of years with consistent results.

**3.4 Standards** Primary standards are obtained from the International Atomic Energy Agency, Vienna, Austria, and certified by NIST (National Institute of Standards and Technology, formerly U.S. National Bureau of Standards) or directly from NIST. Secondary standards are obtained from commercially available sources recognized in the industry. Internal Reference standards are prepared by direct calibration against primary and secondary standards.

**3.5 Duplicate Samples** Duplicate analyses are performed approximately every tenth analysis. This duplicate sample analysis is performed approximately five analyses after the check/reference sample analysis is performed. Therefore, for a particular analysis procedure, a test of the method is performed every five analyses. This assures that at least 20% of all analyses are for maintaining QA/QC.

**3.6 Specific Routine Procedures to Assess Performance** Standard reference samples, chosen to match the submitted samples as closely as possible, in conjunction with duplicate samples and check samples, provide a matrix for performance evaluation. Control charts of replicate analytical data for reference samples are kept for each analytical method practiced routinely. Control charts are used to check the performance of an instrument and/or analytical technique.

Control charts for replicate samples are kept as tables and/or graphs. Graphs are displayed on the wall and data is plotted when measured to see if it falls within a predetermined acceptable range and to monitor for long term changes or trends. If a problem is detected with the reference sample, then the problem is first addressed by checking the integrity of the sample itself. Other reference samples are analyzed to determine if the problem persists. If reference sample integrity is verified, further diagnostic testing is carried out until the cause of the discrepancy is identified.

Isotech willingly participates in round-robin testing whenever the opportunity arises and recently participated in a hydrogen isotope study sponsored by the Finnigan Corporation. Cross-checks with the Illinois State Geological Survey are carried out frequently. Three natural gas standards set up by the International Atomic Energy Agency (IAEA) and now maintained by NIST are periodically analyzed. A supply of these standards is maintained and clients are encouraged to include one of these standards as a sample to be analyzed. Instrument calibration is carried out whenever analysis of internal standards and check samples suggests a potential problem.

**3.7 External Quality Control Checks** Blind duplicates, check samples, blanks, and spiked samples may be submitted by the client, and this practice is encouraged.

## **4. ANALYSES AND ANALYTICAL RESULTS**

**4.1 Data Reduction and Reporting** Calculations made in reducing raw data to reportable form are verified (preferably by a second person) before reporting the results to the client. If a computer program is used to perform calculations, the accuracy of the input data is verified by comparison with the raw data. In all cases where computer programs are used to make the calculations, the person making the calculations verifies that the proper program is used. Data reduction and calculation is performed automatically by the computers which control the instruments. Reported results are verified relative to the computer printouts. This verification involves copying the value from the printout to a report format and is generally performed by the same person who performed the analyses.

**4.2 Hard Copy and Electronic Data Deliverables** Normally, final data is emailed to clients as an Excel workbook file, and also a PDF version of the data. Depending on the sample type, hard copy reports can be either a single page per sample, or can be in tabular format with multiple samples per page. Hard copy reports are mailed to clients, unless clients indicate that the email versions are sufficient for their needs. Upon request, CD's will be submitted to clients in addition to the hard copy reports. Also, appropriate graphs will be provided upon request. Compositional analyses for natural gas samples are normalized to 100% when the Analysis Report is generated. Upon request a QA/QC report containing results for all check samples and duplicates as well as copies of raw data can be provided at additional cost.

**4.3 Documentation** All laboratory notes, observations, calibrations, manual calculations, and any other pertinent information are kept in bound laboratory notebooks or other secure recording medium. Computer programs used for data storage, retrieval, and calculations, which are developed within Isotech Laboratories, Inc., are documented well enough that someone not intimately familiar with the program development, but who is familiar with the programming language, can understand the operation of the program. Printed and dated copies of the current version and each previous version (insofar as possible) of the program are kept in the developer's files. These copies remain at and are the property of Isotech, should the developer leave employment of Isotech Laboratories, Inc. Electronic backup copies of currently-used computer programs are securely kept by the program's developer or principal user. Computer software provided by the instrument manufacturers that reduces raw data and calculates results have been checked by doing the calculations manually. Backup copies of analyses databases are made periodically. The frequency of making backup copies depends on the frequency of updating the database, but the minimum frequency for making backup copies is weekly. All laboratory notebooks, data, computer programs, computerized databases, and any other means of recording data, observations, calculations, and other pertinent information developed at or on behalf of Isotech, remain the property of Isotech Laboratories, Inc., unless otherwise designated by the Board of Directors of Isotech Laboratories, Inc.

**4.4 Hard Copy Data Files and Storage** All pertinent paperwork associated with each batch of samples is stored in the client files. Typical paperwork can include chain of custody records, client analysis requests, email communication to/from clients regarding samples, final data, and cover letter mailed to client with final data. Data files are kept indefinitely unless clients request that we dispose of them.

## **5. MAINTENANCE AND REPAIR**

**5.1 Instruments** Each instrument or machine used to produce quantitative analysis results, or leading up to their production, undergoes periodic preventive maintenance according to manufacturer's instructions, or some established preventive maintenance schedule. Preventive maintenance may be done by laboratory personnel, manufacturer's representative, or a qualified third-party contractor, depending on the abilities of the laboratory operator and the complexity of the equipment. Records of repairs and preventive maintenance are kept by the appropriate laboratory personnel in files or notebooks. Records of equipment problems and solutions are kept in files or notebooks. The analyst is the person best qualified to recognize when the instrument or machine they operate is in need of repair, or the method they practice is in need of corrective action. They are aided in this monitoring by control charts. Corrective action is needed when predetermined limits for data acceptability are exceeded. Analysts are also to use their experience and scientific judgment in deciding when corrective action is needed.

**5.2 Other Equipment** Other laboratory equipment such as vacuum pumps, ovens, test meters and non-instruments such as glassware are maintained by Isotech personnel. In most cases this is performed by the same person who utilizes the equipment for analysis. Visual checks backed

by mechanical and electronic gauges provide constant maintenance checks directly to the operators.

## **6. REVIEW**

**6.1 Analytical Review** At the time of each analysis or sample preparation, the staff chemist performing the analysis reports anomalies to the Laboratory Manager, who is the primary QA/QC officer. Staff chemists are all trained on a variety of techniques and work closely together. Constant communication between staff members results in most problems being addressed when they occur. Unusual problems are brought to the attention of the Laboratory Director. Whenever possible, a sample that is questionable for any reason is re-analyzed to verify results, regardless of when the sample was analyzed initially. This means that more than 10% of samples will be duplicates if the data appears to be unusual in any way.

Before final reports are printed, data is checked to verify that the final data agrees with the raw printouts, and raw percentages for compositional analyses are checked to ensure that all components are identified. Reproducibility of duplicate isotopic samples is compared to stated precision limits. Analytical data is reviewed for anomalies by both the QA/QC Officer and the Laboratory Director prior to reporting.

**6.2 Standard Operating Procedures (SOP's):** These procedures are developed from specific analytical methods for operating specified equipment and supplies to obtain high quality data reflective of each sample analyzed. In addition to revisions due to procedural or equipment changes these SOP's are reviewed by the Laboratory Manager annually.

## **7. QA/QC PROBLEM REPORTING**

**7.1 Responsibilities** QA/QC is the responsibility of every person who collects or analyzes samples. If any Isotech Laboratories, Inc. employee observes any QA/QC problem, that employee will discuss the problem with the analyst, QA/QC officer, or Isotech Laboratories, Inc. Board Member. No negative action will be ever be brought against nor will accrue to any staff member who reports QA/QC problems.

## **8. SUBCONTRACT POLICY**

Samples for analysis of  $^{14}\text{C}$  (radiocarbon) are converted to purified carbon dioxide and then submitted to an established radiocarbon dating laboratory for the final analysis. When analyses are requested for which Isotech does not have either the necessary equipment or expertise to provide high quality results, these analyses too may, with the knowledge of the client, be submitted to a subcontract laboratory. Only established, reputable laboratories which maintain strict QA/QC control are utilized. All samples are prepared and packaged using techniques that have been recommended or approved by the subcontract laboratory. Analysis of reference



samples and standards is the responsibility of the subcontract laboratory. Duplicate analyses of samples submitted to a subcontract laboratory should be requested by the client and will be charged as regular samples.

## APPENDICES: ANALYTICAL PROCEDURES

### I. Sample Preparation Procedures for Stable Isotope Analyses

#### A. Procedures for Stable Isotope Analysis of Water Samples

##### 1. $\delta^{13}\text{C}$ (Carbon Isotope Analysis) of Dissolved Inorganic Carbon (DIC)

###### Equipment and Supplies

Vacuum pumps and gauges  
Glass and metal vacuum system  
Dry ice  
Isopropyl alcohol  
Liquid nitrogen  
Phosphoric acid  
Gas-Oxygen torch

Method/Procedure The  $\delta^{13}\text{C}$  of DIC is determined by injecting up to 20 ml of sample water into an evacuated 60 ml serum bottle containing 2 ml of 85% phosphoric acid and a magnetic spin bar. Sample size is determined based on alkalinity, which is measured by titration with 0.1N HCl.

The sample is stirred for a minimum of 15 minutes and then connected to the vacuum system via a needle port. The hypodermic needle is embedded into the stopper and the air within the needle port is evacuated. The needle is then inserted completely through the stopper. The  $\text{CO}_2$  generated is liberated from the water and transferred through a trap cooled in a dry-ice/isopropyl-alcohol mixture (for  $\text{H}_2\text{O}$  removal) to a U-trap which is cooled in liquid nitrogen. The sample is constantly stirred to ensure that all  $\text{CO}_2$  is liberated from the water. All residual gases are pumped away through the vacuum system. The  $\text{CO}_2$  is transferred into a Pyrex cold finger for yield determination by placing a Dewar of dry ice slush on the U-trap to liberate the  $\text{CO}_2$  and placing a Dewar of liquid nitrogen on the cold finger to collect the  $\text{CO}_2$ . The sample is sealed into the cold finger and the liquid nitrogen Dewar is removed to allow the sample to sublime. The yield is calculated from the pressure reading on a digital manometer connected to the cold finger.

The  $\text{CO}_2$  is then collected in  $\frac{1}{4}$ " OD Pyrex tubing by transferring the purified  $\text{CO}_2$  into the seal tube with liquid nitrogen. The tube is fused shut with a gas-oxygen torch and tagged with a piece of label tape for mass spectrometric analysis.

Maintenance The system is thoroughly evacuated between samples. Vials are washed and dried.

Replication At a minimum, every tenth analysis is a replicate.

Calculation Calculations are performed by the software on the IRMS (Isotope Ratio Mass Spectrometer) at the time of final analysis.

Documentation All procedural tests and verifications performed are recorded in bound maintenance log books. All sample data including the date prepared with analyst identification are recorded on laboratory log sheets and in bound log books.

## **2. $\delta\text{D}$ (Hydrogen Isotope Analysis) and $\delta^{18}\text{O}$ (Oxygen Isotope Analysis) of $\text{H}_2\text{O}$**

### Equipment

3mL syringes

0.2 micron syringe filters

2mL glass vials with septum caps

Picarro CRDS (cavity ringdown spectrometer) model L1102-i fitted with a Leap autosampler

### Method/Procedure

Water samples are individually filtered into 2mL vials with 0.2 micron syringe filters. If samples are high salinity brines, they should be vacuum distilled prior to loading. The vials are then loaded onto trays which are installed on the autosampler. Samples are analyzed by the CRDS in replicate in accordance with the manufacturer's recommendation.

Reference Sample Two reference water samples are used to verify accuracy and reproducibility. These reference waters are analyzed approximately every tenth analysis. Performance is also periodically checked by direct analysis of primary reference standards obtained from IAEA or NIST.

### Replication

At a minimum, every tenth sample analysis is a replicate.

### Calculation

Calculations are performed by the software on the CRDS at the time of analysis.

### Documentation

All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared with analyst identification in bound log books.

### 3. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (Nitrates)

#### Equipment and Supplies

Filter paper  
Glass filtration apparatus  
1N HCl  
 $\text{BaCl}_2$   
Borosilicate glass balls  
Hot Plate  
Cation exchange resin  
Anion exchange resin  
1N HBr  
 $\text{Ag}_2\text{O}$   
DI Water  
Flasks  
Stirbars  
Glass funnel  
Freezer  
Oven  
Freeze-dryer  
Teflon beakers

Method/Procedure Nitrate is extracted from groundwater samples and converted into  $\text{AgNO}_3$  using ion-exchange techniques. Samples are filtered and pH adjusted to 1-3 using 1N HCl boiled to final volume of 250 ml.  $\text{BaCl}_2$  is added to remove dissolved sulfates. The sample is poured into separatory funnels and passed through a pretreated cation exchange column. The sample is then passed through the anion column, where nitrate is held within the column. 1N HBr is added, and the eluate collected, diluted with 20mL DI water, and  $\text{Ag}_2\text{O}$  is added. The sample is filtered, frozen in a Teflon beaker, and placed in a freeze drying vacuum oven until only the  $\text{AgNO}_3$  crystals remain. The crystals are then analyzed using for  $^{15}\text{N}$  using an EA and isotope ratio mass spectrometer (IRMS) and the  $^{18}\text{O}$  values measured using a TCEA-IRMS.

### **B. Procedures for Stable Isotope Analysis of Gas Samples**

#### **1. $\delta^{13}\text{C}$ and $\delta\text{D}$ (Carbon and Hydrogen Isotope Analysis) for Hydrocarbon Gases, Offline Prep Systems**

#### Equipment and Supplies

3 SRI 8610C Gas chromatographs  
Evacuated transfer system  
Copper oxide combustion furnace

Dry ice  
Isopropyl alcohol  
Liquid nitrogen  
Electronic manometer  
Electronic vacuum gauge  
Helium  
Oxygen  
Gas-oxygen torch

Method/Procedure The determination of carbon and hydrogen isotopic ratios for hydrocarbons in gas mixtures (e.g. natural gas) requires a sample preparation system capable of first separating the individual hydrocarbons and then quantitatively converting them into carbon dioxide (CO<sub>2</sub>) and water for mass-spectrometric analysis. There are 2 systems utilized for processing natural gases. The systems employed are helium purged flow systems consisting of two major units.

The first unit consists of sample injection syringes, SRI 8610C gas chromatographs, a personal computer, and several flow-control valves. This configuration separates the hydrocarbon of interest from the sample and channels it into the combustion-collection unit. The second unit is the combined combustion-collection unit which includes quartz combustion tubes filled with cupric oxide (CuO), and vacuum lines. This system converts the hydrocarbon of interest into CO<sub>2</sub> and water, which are then collected and purified for isotopic analysis.

Samples can be analyzed from a variety of different sampling containers such as high-pressure cylinders, gas bags, or vacutainers. The sample is expanded into the injection syringes which have been pre-set to the desired volume, and adjusted to atmospheric pressure. Once the sample is loaded into the injection syringe, the separation is automated by both a personal computer and on-board computers within the gas chromatographs. Once a run is initiated, the GC software controls valves to the injection syringes, and controls the valves to the separation columns.

The sample hydrocarbon is flowed through a copper oxide combustion furnace set at 850°C utilizing helium as the carrier gas. On the downstream side of the furnace, both the carbon dioxide and the water of combustion are collected in a liquid nitrogen-cooled trap. Once the entire sample has been collected, the helium carrier gas is evacuated. The carbon dioxide is then transferred into a cold finger attached to a digital manometer for yield measurement by placing a dewar of dry ice slush on the collection trap to liberate the CO<sub>2</sub> while maintaining the water in the collection trap. Once all of the CO<sub>2</sub> has been collected in a cold finger, the valve to the cold finger is closed and the liquid nitrogen is removed to allow the CO<sub>2</sub> to sublime for yield determination.

The water of combustion is then transferred into a 12-inch length of ¼" OD Pyrex tubing that has been sealed at one end and contains a weighed quantity of zinc turnings. The zinc is prepared by evacuating and heating to 400°C for at least 5 minutes while open to vacuum. Once the sample water has been completely transferred into the sample tube and frozen with liquid nitrogen, the sample tube is sealed off with a torch for later mass spectrometric analysis.

After the water has been sealed off, the pressure reading on an electronic pressure gauge connected to the coldfinger is used to calculate the yield of CO<sub>2</sub>, and this is recorded in the lab notebook. The CO<sub>2</sub> is then transferred into ¼" OD Pyrex tubing and sealed with a torch for later mass spectrometric analysis.

Maintenance The packed columns used for GC separation are backflushed after every sample and serviced when the peak separation decreases. This service consists of baking at manufacturer's recommended temperature and time. During the heating and cooling process, O<sub>2</sub> is flowed through the copper oxide combustion furnaces to regenerate the CuO. This conditioning process is completed each day samples are analyzed. The transfer/collection system is thoroughly evacuated between samples. Valve o-ring seals within the evacuated transfer system are replaced as required.

Reference Samples The system is tested by analyzing a reference sample every tenth analysis performed.

Replication A duplicate analysis of one of the samples is performed approximately every tenth analysis. This duplicate analysis is performed approximately five analyses after the reference sample analysis is performed. Therefore, a test of the system operation is performed every five analyses.

Calculation The expected yield is calculated from the injection volume and the hydrocarbon concentration

Documentation All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared with analyst identification are recorded on laboratory log sheets and/or in bound log books. Digital copies of all chromatograms are stored and backed up regularly.

## **2. $\delta^{13}\text{C}$ (Carbon Isotope Analysis) of CO<sub>2</sub>, Offline Prep Method**

Method/Procedure Preparation of samples for measurement of the  $\delta^{13}\text{C}$  of CO<sub>2</sub> is performed on the same system as the hydrocarbons. The procedure is identical to that for the hydrocarbons, with two exceptions. First, CO<sub>2</sub> does not pass through a combustion furnace; gas is channeled directly from the GC outlet to the collection trap. Second, there is no water of combustion. Therefore, the collection/purification system is slightly smaller as it has only one sample tube, and all steps related to collecting the water of combustion are omitted.

## **3. GC-C-IRMS systems, $\delta^{13}\text{C}$ , $\delta\text{D}$ , and $\delta^{15}\text{N}$**

### **Equipment and Supplies**

HP6890 GC interfaced to ThermoFinnigan Delta Plus Advantage  
HP6890 interfaced to Thermo Electron Delta V Plus  
HP 6890 interfaced to Thermo Scientific Delta V Plus

## CTC Analytical GC PAL autosampler

### Method/Procedure

GC-C-IRMS systems, also referred to as “online” or “continuous flow”, consist of an Agilent 6890 GC combustion unit and Finnegan GCCIII interfaced with a mass spectrometer (Delta V Plus or Delta Plus Advantage), and are used to analyze the carbon isotopic value of hydrocarbon components in gas samples. Samples are injected into the HP6890 split/splitless injector either manually, or using customized GC PAL auto-samplers. The hydrocarbon components are separated by the GC column in the HP6890, and each individual component slated for isotopic analysis is combusted in a combustion furnace supplied by the instrument manufacturer. The resultant CO<sub>2</sub> is introduced directly into the mass spectrometer, and Finnegan’s Isodat software is utilized for peak detection and quantification.

Hydrogen isotopic values for methane are completed using the same system, but the gas is channeled through a high-temperature pyrolysis furnace instead of through the combustion furnace. The pyrolysis furnace converts methane into H<sub>2</sub> and carbon, and the H<sub>2</sub> gas is introduced directly into the mass spectrometer.

Nitrogen isotopic data for elemental nitrogen (N<sub>2</sub>) is generated using the same system, with one key difference: the temperature on the combustion reactor is reduced so that the N<sub>2</sub> is not oxidized.

### Maintenance

Septa on the GC inlet system are replaced daily when the system is operational. Pyrolysis and combustion tubes are replaced as needed. Combustion tubes are oxidized daily during analysis sequences.

### Reference Samples

Reference gases are analyzed at the start of each analysis sequence, and then at least 10% of all analyses during a sequence are check samples.

### Replication

At least 10% of client samples are analyzed in duplicate.

## **C. Procedures for Stable Isotope Analysis of Organic Solids and Liquids**

### Equipment and Supplies

Carlo Erba Elemental Analyzer connected to a Finnigan Delta S Mass Spectrometer  
ThermoElectron TCEA interfaced to a Thermo Electron Delta V Plus Mass Spectrometer

Elementar EL Vario III interfaced to a Thermo Scientific Delta V Plus Mass Spectrometer

Method/Procedure The determination of carbon, nitrogen, oxygen, hydrogen, and sulfur isotopic ratios for organic solids and liquids is accomplished by combustion or pyrolysis of the materials for mass-spectrometric analysis. The systems employed are standard elemental analyzers with carousel auto samplers, connected to isotope ratio mass spectrometers through an interface supplied by the manufacturer. The combustion products of interest from the elemental analyzers are: carbon dioxide (CO<sub>2</sub>) for carbon isotope analysis, N<sub>2</sub> for nitrogen isotope analysis, and sulfur dioxide (SO<sub>2</sub>) for sulfur isotope analysis. Oxygen and hydrogen isotopic ratios are analyzed on the TCEA, which converts hydrogen from the organic materials to H<sub>2</sub> gas for hydrogen isotopic measurements, and oxygen within the organic materials is converted to carbon monoxide (CO) for oxygen isotope analysis. This system in its entirety was purchased expressly for analysis of these samples.

Samples are weighed on a Mettler balance and loaded into a standard EA tin capsule for carbon, nitrogen, or sulfur isotopic analysis, or into a silver capsule for oxygen or hydrogen isotopic analysis. Once the samples are loaded into the EA, a run is started and all instrument control is done by software provided by the MS manufacturer. Samples are combusted as per normal EA operating procedures, and the CO<sub>2</sub>, N<sub>2</sub>, and SO<sub>2</sub> are separated by the EA. Similarly, the pyrolysis products H<sub>2</sub> and CO from the TCEA are separated within the instrument. The vents of the EA and the TCEA are connected to the mass spectrometers via the interface, where a small portion of the EA or TCEA output flows directly into the MS. The MS measures the isotopic value of the component of interest (CO<sub>2</sub>, N<sub>2</sub>, SO<sub>2</sub>, CO, or H<sub>2</sub>) and the final isotopic value is generated by software provided by the manufacturer.

Maintenance Ash is removed from the top of the combustion column in the EA or the top of the pyrolysis reactor in the TCEA as directed by the manufacturer, or when peak tailing becomes apparent. Combustion and reduction furnaces in the EA are replaced at appropriate intervals as outlined by the dealer, or when peak shape deteriorates. The TCEA contains glassy carbon, which is periodically replaced.

Reference Samples The systems are tested by analyzing at least one reference at least once per batch of 25 samples loaded into the auto sampler. A blank is also run at the start of each batch.

Replication Approximately 10% of all samples analyzed are replicates.

Documentation All final data including the date analyzed are recorded on laboratory log sheets and/or in bound log books. Digital copies of chromatograms are stored and backed up regularly.

## **II. Sample Preparation Procedures for Radiogenic Isotope Analyses**



## A. Procedures for Radiogenic Isotope Analysis of Gases

### 1. $^{14}\text{C}$ (Radiocarbon) and $^3\text{H}$ (Tritium) in $\text{CH}_4$ (Methane) by Radiometric Analysis

#### Equipment

Peristaltic pump  
Flow meters  
Gas regulators  
Vacuum gauge  
Molecular sieve trap  
High temperature tube furnaces  
Quartz combustion chamber  
Vacuum traps and gauges  
Vacuum pumps  
Mercury manometer

#### Method/Procedure

##### 1.1 Methane Combustion

The system used for tritium ( $^3\text{H}$ ) analysis of methane and for radiocarbon ( $^{14}\text{C}$ ) analysis of methane consists of a peristaltic pump, a  $\text{CO}_2$  removal unit, and a sample combustion/collection flow unit. The  $\text{CO}_2$  removal unit includes a trap filled with molecular sieve and an ascarite backup trap. The combustion/collection unit is composed of a tube furnace, an inner and an outer quartz combustion tube which are interconnected through an orifice located at the tip of inner tube, a flow control valve, and a series of gas purification and collection traps. The system is attached to a vacuum manifold.

The molecular sieve is baked and evacuated to  $350^\circ\text{C}$  before each use to ensure that all absorbed gases are removed from the trap. After the molecular sieve is cooled to room temperature, the system is first evacuated, and then pressurized with argon. Oxygen is then introduced into the outer combustion tube which is partly filled with cupric oxide ( $\text{CuO}$ ) and placed in a tube furnace preheated to  $850^\circ\text{C}$ . After the flow is established, the gas sample enters the system through a flow control valve (if the sample is above atmospheric pressure) or is pumped in slowly by a peristaltic pump (if the sample is at or below atmospheric pressure).  $\text{CO}_2$  associated with the sample is absorbed by the molecular sieve and removed from the sample quantitatively. Methane in the sample is then carried by argon through the inner combustion tube and ignited at the tip of the tube where oxygen is supplied.

The water of combustion is collected in a trap immediately after the combustion furnace. This collection trap is heated under vacuum prior to each analysis to ensure that there is no cross-contamination between samples. To collect the sample water, the trap is immersed in a dry ice/isopropanol bath. Once the entire sample has been combusted, the frozen water of combustion is melted and transferred to a glass vial to await tritium analysis.

The  $\text{CO}_2$  formed by combustion is collected in two liquid nitrogen cooled traps, measured volumetrically, and transferred into a storage cylinder. Storage cylinders are effectively leak-tested during each use by evacuation prior to transferring the sample  $\text{CO}_2$ . Each cylinder is tagged with sample identification and is forwarded to a subcontractor for  $^{14}\text{C}$  analysis along with a chain-of-custody form.

If the yield of  $\text{CO}_2$  is less than one liter, the sample is diluted to approximately one liter with  $^{14}\text{C}$  free  $\text{CO}_2$  prepared from the combustion of natural gas. The dilution gas has been analyzed to verify that it is  $^{14}\text{C}$  free, and found to be statistically indistinguishable from background. The volume of the sample and the volume of the dilution gas are precisely measured with a mercury manometer. The dilution factor measured is used in the final calculation of the  $^{14}\text{C}$  activity.

## 1.2 Tritium Analysis

The water of combustion from methane samples is ready to be analyzed in the liquid scintillation (LS) spectrometer. There is no pre-treatment necessary for the sample, as it is essentially distilled water when it is collected.

The scintillation counting vials are prepared by pipetting 10 ml of commercial scintillation cocktail into a 20 ml plastic vial and then weighing to  $\pm 1$  mg. The sample is then pipetted or poured into the counting vial and the vial is re-weighed. If the amount of sample is less than 10ml, then tritium-free water is added to bring the total volume of water to about 10ml. Details of the tritium analysis procedure are given later in this document.

Maintenance After each sample, the molecular sieve is baked and evacuated at  $350^\circ\text{C}$ . The vacuum system is thoroughly evacuated to remove all residual gas and water vapor after each sample. The water trapping system is disassembled and thoroughly dried and evacuated after each sample.

Calibration/Standardization Gas storage volumes have been calibrated using known quantities of carbon dioxide gas. No further standardization of this system is necessary. Calibration and standardization of the final  $^{14}\text{C}$  analysis is performed by the subcontracted laboratory.

Replication and Reference Samples Replicate or reference sample analysis for these analyses are performed only when requested and supported by the client.

Calculation Yields are calculated by comparing the volume of  $\text{CO}_2$  generated and the weight of the water collected to the amount expected based on the amount of  $\text{CO}_2$  collected.  $^{14}\text{C}$  concentrations are determined by the subcontracted laboratory and corrected for isotope fractionation by Isotech's database program.

## 2. $^{14}\text{C}$ (Radiocarbon) in $\text{CO}_2$ by Radiometric Analysis

### Equipment

Same as for  $^{14}\text{C}$  of  $\text{CH}_4$

Method/Procedure After the  $\text{CO}_2$  from methane has been collected as described in the previous section, the expansion cylinder and the collection traps are evacuated. The argon carrier gas trapped in the molecular sieve is evacuated and then a tube heater is placed on the molecular sieve trap. The trap is heated to  $350^\circ\text{C}$  to liberate the sample  $\text{CO}_2$  from the molecular sieve. The  $\text{CO}_2$  is then transferred via a shunt to the  $\text{CO}_2$  collection system. The  $\text{CO}_2$  is collected in a liquid nitrogen-cooled trap. Once the sample has been transferred into the collection traps, the sample yield is measured and the sample is transferred into a storage cylinder using the same method as for methane. The purified  $\text{CO}_2$  is then submitted to a subcontract laboratory for radiometric analysis of  $^{14}\text{C}$ .

### **3. $^{14}\text{C}$ (Radiocarbon) in $\text{CH}_4$ and $\text{CO}_2$ by Accelerator Mass Spectrometry (AMS)**

Equipment:

Same as for  $\delta^{13}\text{C}$  of  $\text{CO}_2$  and  $\delta^{13}\text{C}$  of Hydrocarbons.

Method/Procedure:

The same method is employed for sample preparation as for  $\delta^{13}\text{C}$  of either  $\text{CH}_4$  or  $\text{CO}_2$ . Once the purified  $\text{CO}_2$  has been sealed into Pyrex tubing, the tube is tagged with a piece of label tape and sent to the subcontractor along with a chain of custody form for  $^{14}\text{C}$  analysis. When there is only enough material available for one sample preparation, the  $\delta^{13}\text{C}$  is first determined by MS analysis. Then the sample is frozen back out of the MS with liquid nitrogen and sealed into the same Pyrex tubing before shipment to the subcontractor. A longer sample tube is used on the initial sample preparation to ensure that there is sufficient tube available for sealing after MS analysis. The sealed sample is then submitted to a subcontract laboratory for  $^{14}\text{C}$  determination by accelerator mass spectrometry.

## **B. Procedures for Radiogenic Isotope Analysis of Water**

### **1. $^{14}\text{C}$ (Radiocarbon) in dissolved inorganic carbon (DIC) by Accelerator Mass Spectrometry (AMS)**

#### Equipment

Same as for  $\delta^{13}\text{C}$  of DIC.

#### Method/Procedure

The same method is used as for  $\delta^{13}\text{C}$  of DIC. Once the purified  $\text{CO}_2$  has been sealed into Pyrex tubing, the tube is tagged with a piece of label tape and sent to the subcontractor, along with a chain of custody form, for  $^{14}\text{C}$  analysis. When there is only enough material available for one sample preparation, the  $\delta^{13}\text{C}$  is first determined by MS analysis. Then the sample is frozen back out of the MS with liquid nitrogen and sealed into the same Pyrex tubing before shipment to the subcontractor. A longer sample tube is used on the initial sample preparation to ensure that there is sufficient tube available for sealing after MS analysis. The sealed sample is then submitted to a subcontract laboratory for  $^{14}\text{C}$  determination by accelerator mass spectrometry.

### **2. $^3\text{H}$ (Tritium) in $\text{H}_2\text{O}$**

#### Equipment

Vacuum pumps and gauges  
Distillation column  
Electrolytic enrichment cells  
Electrolysis power source and cooling system  
Liquid scintillation counting system  
Assorted chemicals and glassware  
Dry ice/ isopropyl alcohol  
Drying oven

#### Method/Procedure--Direct Counting of Higher Tritium Content Water (greater than 15 TU).

Approximately 15ml of the water sample is treated with 0.1 M  $\text{KMnO}_4$  at  $70^\circ\text{C}$  for about an hour. This sample is then vacuum distilled. Ten ml of the distillate is accurately weighed and mixed with 10ml of an appropriate organic scintillator cocktail in a 20ml plastic vial and counted in a liquid scintillation spectrometer for 1000 minutes. Background and a NIST standard are also similarly counted and the tritium content calculated.

#### Method/Procedure--Enrichment of Lower Tritium Content Water (less than 15 TU).

About 300 ml of the water sample is conventionally distilled to near completion. Exactly 200g is added to an enrichment cell along with 2ml of 9M tritium-free sodium hydroxide and is electrolytically enriched down to about 11-13 ml (final weight is exactly determined), and then neutralized with carbon dioxide for 20 minutes. The enrichment procedure is carried

out under conditions of about 2°C and constant voltage of 4V. Ten ml of the enriched sample is accurately weighed and mixed with an appropriate organic scintillator cocktail in a 20 ml plastic vial and counted in a liquid scintillation spectrometer for 1000 minutes. Background and a NIST standard are also similarly counted and the tritium content calculated.

General QA/QC Procedures include critically reviewing TU/cpm/g of NIST standard versus existing data, critically reviewing background cpm versus existing data, and comparing data from splits of NIST and other samples with outside established laboratories. A criteria of exceeding 1 sigma limits from existing data triggers investigation of possible errors. Electrolytic enrichment cells are calibrated using working standards approximately every 6 months, or whenever duplicates prepared in different cells suggest a possible change in enrichment factor.

Maintenance The vacuum system is thoroughly evacuated between samples. All glassware and electrolytic cells are cleaned with deionized water and baked out at about 130° C between samples.

Replication At a minimum, every tenth analysis is a replicate. Periodically a blind split is sent to another established tritium analysis laboratory for check purposes.

Reference Sample A NIST water standard (a dilution of NIST 4361B) is used for each sample set to verify accuracy and reproducibility. A glass-sealed high tritium sample is routinely checked to verify that the counter is operating satisfactorily. QA/QC plots are maintained for both standard and background counts using deviation of 1 sigma as a criteria for a more detailed evaluation of the data.

Calculation Calculations are performed utilizing a spreadsheet to calculate tritium concentration in TU on the date counted.

Documentation All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared, with analyst identification, are recorded on laboratory log sheets or in bound log books.

### III. Dual Inlet Mass Spectrometric Analysis

#### A. Measurement of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ in $\text{CO}_2$

Equipment Finnigan MAT Delta S Isotope Ratio Mass Spectrometer

Method/Procedure Because  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  analyses are performed simultaneously, the procedure described here generates both measurements. A mass spectrometric analysis involves comparisons of a sample to a reference standard; in this case the comparisons are measurements of mass 44, 45, and 46, giving the both the oxygen and carbon isotopic compositions. This is accomplished by a dual inlet system where the sample and the reference standard are measured alternately. At the beginning of each day, a reference standard is introduced into the standard side of the inlet system, and this gas is generally used for the entire session. There are two different reference standards in aluminum cylinders which are permanently mounted on the MS inlet system. The sample to be analyzed against the standard is introduced into the system via an evacuated inlet system and tube-cracker. With the inlet system fully evacuated, the sample (which is sealed into 1/4" Pyrex tubing) is introduced by breaking the glass sample tube and allowing the sample to fill a variable volume bellows. Once the sample has been introduced into the MS, the actual analysis is computer controlled using equipment obtained from the manufacturer. Each analysis is given a specific reference name and/or number, utilizing the lab number as the primary reference. Final results are calculated by the manufacturer's software, and are stored on the hard drive of the computer, recorded in a bound lab notebook, and stored as the computer generated printout.

Maintenance The source region of the MS is periodically disassembled and cleaned. The filament is replaced as needed. Oil levels in mechanical vacuum pumps are checked frequently and maintained at the proper level. Turbomolecular pumps are lubricated according to the manufacturer's recommendations.

Calibration/Standardization The first analysis of each session is a zero enrichment, where the working standard is analyzed against itself to check machine stability. Isotope ratio determination involves multiple direct comparisons of the sample to a reference standard (generally at least 6 comparisons). Stable carbon and oxygen isotope compositions are always reported as the difference between the ratios of the two isotopes of interest in the sample and the ratio in a primary reference standard. That is,

$$\delta X_{(\text{sample})} = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 1000$$

Where X represents the isotope of interest,  $^{13}\text{C}$  or  $^{18}\text{O}$ , and R represents the ratio of  $^{13}\text{C}/^{12}\text{C}$ , or  $^{18}\text{O}/^{16}\text{O}$ . The  $\delta$  value is expressed in terms of per mil (‰), or parts per thousand.

In practice, the difference between the sample and an internal reference standard is measured and then the value relative to the primary standard is calculated by the instrument manufacturer's software. Two internal reference standards are used at Isotech, both of which have been calibrated multiple times over the past 20 years relative to several standards (graphite, oil, carbonates, waters, etc.) available from the International Atomic Energy Agency and the National Institute of Standards and Technology, in at least two different laboratories and on up to five different mass spectrometers. Standardization of the mass spectrometer involves analyzing one the reference standards against the other (the reference standard used for the actual analysis is chosen according to the types of samples to be analyzed). This standardization is carried out at least once each day that analyses are to be conducted. In the rare event that the value obtained differs by more than 2 standard deviations from the expected value, the standardization is repeated with new aliquots of the reference standards. If the difference persists, the calibration of the reference gases is checked by having them analyzed by another laboratory, or by recalibrating them relative to NIST or IAEA standards.

Replication Because of replicate sample preparations, at least 10% of all analyses are replicates.

Reference Samples Because 10% of all samples prepared for stable isotope analysis are check samples or reference samples which have been previously analyzed, these samples also serve as check samples for the mass spectrometer.

Calculation All calculations are performed by the software obtained from the manufacturer.

## **B. Measurement of $^2\text{H}/^1\text{H}$ (Deuterium/Hydrogen) in $\text{H}_2$**

### Equipment

Finnigan Delta Plus XL isotope ratio mass spectrometer

Aluminum heating block

Personal computer

Method/Procedure The  $\text{H}_3$  factor, which is the portion of the mass 3 signal attributable to  $^1\text{H}-^1\text{H}-^1\text{H}$  (instead of  $^2\text{H}-^2\text{H}$ ), is determined before each run early in the day and periodically throughout the day based on machine performance (if the values start drifting, a new  $\text{H}_3$  factor is determined). The reference standard must be replenished at least once during an 8 hour period.

Water samples for deuterium/hydrogen analysis are sealed into  $\frac{1}{4}$ " Pyrex tubing as  $\text{H}_2\text{O}$ , along with a measured quantity of zinc. Each sample tube is labeled and reacted in a heating block at  $500^\circ\text{C}$  for 35 minutes to generate hydrogen gas. Once the sample has been reacted, it is introduced into the sample side of the MS inlet system and analyzed against the working standard. Each analysis is given a unique label, using the lab number as the primary reference. Once the sample has been introduced into the MS, the analysis is computer controlled. The raw result is calculated by the manufacturer's software and recorded into a bound lab notebook, as well as being stored on computer hard disk and computer generated printout of results.

Maintenance The source region of the MS is periodically disassembled and cleaned. The filament is replaced as needed. Oil levels in mechanical vacuum pumps are checked frequently and maintained at the proper level. Turbomolecular pumps are lubricated according to the manufacturer's recommendations.

Calibration/Standardization The first run each day is a zero-enrichment where the standard is run against itself to check machine stability. Stable hydrogen isotope compositions are always reported as the difference between the ratios of the two isotopes of interest in the sample and the ratio in a primary reference standard. That is,

$$\delta D_{(\text{sample})} = [({}^2\text{H}/{}^1\text{H}_{\text{sample}} - {}^2\text{H}/{}^1\text{H}_{\text{standard}}) / {}^2\text{H}/{}^1\text{H}_{\text{standard}}] \times 1000$$

The  $\delta$  value is expressed in terms of per mil (‰), or parts per thousand.

In practice, the difference between the sample and an internal reference standard is measured and then the value relative to the primary standard is calculated by the instrument manufacturer's software. Two internal reference standards are used at Isotech which have been calibrated relative to several water standards available from the International Atomic Energy Agency and the National Institute of Standards and Technology. Standardization of the mass spectrometer involves analyzing one the reference standards against the other. This standardization is carried out at least once each day that analyses are to be conducted. In the rare event that the value obtained differs by more than 2 standard deviations from the expected value, the standardization is repeated with new aliquots of the reference standards. If the difference persists, the calibration of the reference gases is checked by having them analyzed by another laboratory, or by recalibrating them relative to NIST or IAEA standards. Aliquots of the NIST and IAEA standards are also periodically analyzed as samples as a further check on the calibration of the reference standard.

Replication Because of replicate preparation of samples, at least 10% of all analyses are replicates.

Reference Samples Because 10% of all samples prepared for stable isotope analysis are check samples or reference samples which have been previously analyzed, these samples also serve as check samples for the mass spectrometer.

Calculation All calculations are performed by the manufacturer's computer software. The raw data is then converted to final data using a spreadsheet on a personal computer. The spreadsheets are stored on computer hard disk and a copy is attached to the raw printouts for each batch of analyses.



## IV. Gas Chromatographic Analysis of Gases

### A. Analysis of hydrocarbons

Equipment Carle AGC 400 Gas Chromatograph which was custom designed by the manufacturer for Isotech. The GC is equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors. Data processing is provided by a Nelson Analytical PC Interface coupled with a personal computer.

Method/Procedure At the start of each day, the detectors are turned on and the flow rate of the carrier gas is adjusted to an optimum level. The system is given 30 minutes for the thermistor detector to stabilize before the first sample is analyzed.

All gas sampling cylinders are fitted with a regulator containing a septum on the outlet. Before opening the valve on the cylinder, the air from the regulator is evacuated through a needle port connected to the inlet vacuum. If there is sufficient sample pressure, the outlet pressure is adjusted to approximately 50 psig.

The sample loop on the GC is evacuated to less than 60 microns between each sample. Samples are taken from the cylinder using a gas-lock syringe and injected through a septum into the evacuated sample loop. Air contamination from the syringe needle is evacuated while the loop is still open to the vacuum line. A large enough syringe is used to pressurize the sample loop with gas, and then the loop is adjusted to atmospheric pressure through a tube that is vented under water (to prevent air from leaking back into the vent). Sample identification is entered into the Nelson software and the method is downloaded into the PC interface. The run is then started by pressing a "run" keypad on the GC.

The Carle AGC 400 operates under isothermal conditions, utilizing several different packed columns and valve switching to separate the various components. Instrument configuration was designed by Carle specifically to meet the requirements of Isotech. Helium is used as the carrier gas. All valve switching during the analysis is computer-controlled. The detectors are connected to the PC interface, which converts the analog signal to digital and sends the data to the PC software for processing. The software for the Nelson system does component detection and area integration. The resulting component peak areas are then quantified by the software (given raw percent values) by comparing them to previously run standards. The lab technician checks the raw total for each analysis to ensure that all components have been detected. The raw total can vary from day to day depending on atmospheric pressure, with acceptable raw totals of 97% to 103%. The lab technician also checks all baselines for accuracy from the chromatograms shown on the computer screen. This raw computer record is maintained for each sample corresponding to its individual lab number. The raw percentage values for each sample are downloaded into the main sample database, and are normalized to 100% when the Analysis Report is generated.

Maintenance GC columns are periodically baked out according to manufacturer's instructions. Septa in the sampling valves are replaced as needed.

Calibration/Standardization Approximately 10 different reference standards are used for standardization of the Carle AGC 400 gas chromatograph. These standards were all purchased from Scott Specialty Gases. Most of these standards also contain some of the fixed gases. Normally all 10 are analyzed on the same day during a new standardization to minimize the effects of barometric pressure variations. The concentration for the individual components range from 15ppm to 99% (for methane). Maximum concentrations of other hydrocarbons are 12.6% for ethane, 7% for propane, 3% for butanes, and 1% for pentanes. These concentration ranges cover the majority of natural gases submitted for analysis. For each new standardization, the peak area of each concentration for each compound is inserted into a table within the Nelson software. This table is then accessed by the software, which uses point-to-point interpolation, to determine component concentrations for gas samples during analysis. At least four points are used for each component.

Reference Samples The reference sample used as the 1st run of each day and every tenth sample thereafter is representative of the majority of natural gas samples received for analysis. Reference samples are either created from a single sample or are mixed from several samples to give the desired composition. New reference samples are created before the current sample is depleted, and older reference samples are stored for future analysis and cross checks should problems arise. Data obtained for reference samples and expected results based on previous analyses can be provided as part of a QA/QC report.

Replication Every tenth analysis is a replicate. This replicate analysis is done approximately five samples following the check sample, thus a system check is performed at least every five analyses.

Calculation Each individual component for each sample is manually compared to the computer generated output to insure that the peak was labeled correctly and integrated correctly by the Nelson software.

## **B. Analysis of fixed gases**

Equipment Carle AGC 400 Gas Chromatograph, Carle AGC 100 Gas Chromatograph with dual TCD detectors, and Nelson Analytical GC Interface.

Method/Procedure The procedure for analysis of fixed gases is identical to that for analysis of hydrocarbons, with two exceptions. First, for separation of oxygen and argon, an external column on the AGC 100 is used. This column operates at -78°C, therefore a dewar of dry ice/isopropyl alcohol is placed on the column before each run. At the end of each run, the dewar is removed and the column is warmed to room temperature to allow any other components held on the column to be passed. The column is flushed for 15 minutes between runs while the other

GC is in operation. The second difference is that the Carle AGC 100 is not computer controlled. This means that the technician must control the two valves manually. Both valves are switched to forward flow at the start of each analysis, and the Nelson PC interface is then started. Both valves are switched to backflush at predetermined times. The exact time of the switch is determined by monitoring the "real time" display on the computer screen. The lab technician checks all baselines to verify peak integration.

Maintenance GC columns are periodically baked out according to manufacturer's instructions. The septum on the injection valve is periodically replaced.

Calibration/Standardization Approximately 10 different reference standards are used to standardize the Carle AGC 100 and Carle AGC 400 for compositional analysis of fixed gases. All of these gases were purchased from Scott Specialty Gases. Some of these standards also contain hydrocarbons and are used for standardization of those compounds as well. Normally, all gases are analyzed on the same day during a new standardization to minimize the effects of barometric pressure. The concentration ranges of the standards cover the majority of natural gases submitted for analysis. For each new standardization, the peak area of each concentration for each compound is inserted into a table within the Nelson software. This table is then accessed by the software which uses point-to-point interpolation to determine component concentrations for gas samples during analysis.

Check Sample The reference sample used as the 1st run of each day and every tenth sample thereafter is chosen based on its composition. All reference samples contain at least nitrogen and carbon dioxide, and most also contain hydrogen, helium, and argon. The reference samples are either a single sample meeting the above requirements, or are mixtures of several samples to give the desired composition. New reference samples are created before the current sample is depleted, and older reference samples are stored for future analysis and cross checks should problems arise. Data obtained for reference samples and expected results based on previous analyses can be provided as part of a QA/QC report.

Replication Every tenth analysis is a duplicate. This duplicate analysis is performed approximately five samples following the check sample, thus a system check is performed at least every five analyses.

Calculation Each individual component for each sample is manually compared to the computer generated output to insure that the peak was labeled correctly and integrated correctly by the Nelson software.

## **V. Radiocarbon Analysis of Prepared Samples**

Radiocarbon analyses of purified CO<sub>2</sub> samples prepared by Isotech are currently being subcontracted to either Beta Analytic Inc., Coral Gables, Florida or to Illinois State Geological Survey, Champaign, Illinois. Beta Analytic is the largest commercial radiocarbon dating laboratory in the world. The attached QA/QC plans have been provided by

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